THE SOLUTION COMPOSITION OF SOME ORGANOMAGNESIUM REAGENTS AS INFERRED FROM SPECTROSCOPIC AND COLLIGATIVE PROPERTY STUDIES

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THE SOLUTION COMPOSITION OF SOME ORGANOMAGNESIUM REAGENTS
AS INFERRED FROM SPECTROSCOPIC AND
COLLIGATIVE PROPERTY STUDIES

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TABLE OF CONTENTS

Page

ACKNOWLEDGEMENTS ii

LIST OF TABLES viii

LIST OF FIGURES ix

SUMMARY xii

PART I

THE COMPOSITION OF METHYL- AND TERTIARY-BUTYLMAGNESIUM HALIDES AND THEIR DIALKYL-MAGNESIUM ANALOGS IN DIETHYL ETHER AND TETRAHYDROFURAN AS INFERRED FROM NMR SPECTROSCOPY

Chapter

I. INTRODUCTION 2

Background
Purpose

II. EXPERIMENTAL 6

General Considerations
Solvents
Grignard Reagents
Dimethylmagnesium
Magnesium Halides
Sample Preparation
Nuclear Magnetic Resonance (NMR) Technique
Computer Simulation of Spectra

III. RESULTS 13

Dimethylmagnesium in Diethyl Ether
Methyl Grignard Reagents in Diethyl Ether
Dimethylmagnesium in Tetrahydrofuran
Methyl Grignard Reagents in Tetrahydrofuran
Tertiary-Butylmagnesium Compounds in Diethyl Ether and Tetrahydrofuran

TABLE OF CONTENTS (Continued)

Chapter Page

IV. DISCUSSION 43

General
Concerning the Position of the Schlenk Equilibrium
Concerning the Dynamics of the Schlenk Equilibrium

V. CONCLUSIONS 59

APPENDIX 1: INPUT DATA FOR THE DNMR PROGRAM 61

APPENDIX 2: APPLICATION OF THE WEIGHTED AVERAGE LAW FOR EXCHANGING SYSTEMS TO THE SCHLENK EQUILIBRIUM 64

APPENDIX 3: EFFECT OF THE RAPID DESOLVATION EQUILIBRIUM UPON THE RATE OF INTERMOLECULAR ALKYL EXCHANGE . . . 66

LITERATURE CITED 68

PART II

THE STRUCTURE AND SOLUTION COMPOSITION OF CYCLOPENTADIENYLMETHYLMAGNESIUM IN BENZENE AND ETHER SOLVENTS

Chapter

I. INTRODUCTION 72

Background
Purpose

II. EXPERIMENTAL 76

Synthesis and Analysis
General Procedures
Preparation of Dimethylmagnesium
Distillation of Cyclopentadiene
Preparation of Cyclopentadienylmethylmagnesium Monoetherate
Vacuum Line Technique for Methane Analysis
Physical Studies
Desolvation of Cyclopentadienylmethylmagnesium Monoetherate
Solubility
Alkylation of 4-t-Butylcyclohexanone
Physical Methods of Analysis

TABLE OF CONTENTS (Continued)

Chapter Page

III. RESULTS AND DISCUSSION 81

Solid Phase Studies
Solution Phase Studies

IV. CONCLUSIONS 94

APPENDIX 1: INFRARED SPECTRA OF METHYL-MAGNESIUM COMPOUNDS 98

APPENDIX 2: MOLECULAR ASSOCIATION STUDIES 111

LITERATURE CITED 114

PART III

SOLUTION COMPOSITION AND INTERCONVERSION OF VARIOUS FORMS OF ALKOXY(METHYL)MAGNESIUM REAGENTS

Chapter

I. INTRODUCTION 118

Background
Purpose

II. EXPERIMENTAL 124

Synthesis and Analysis
General Procedures
Preparation of Dimethylmagnesium
Purification of Alcohols
Preparation of Alkoxy(methyl)magnesium Compounds
General
1,1-Diphenylethoxy(methyl)magnesium
t-Butoxy(methyl)magnesium, Kinetic Form
t-Butoxy(methyl)magnesium, Cubane Form
Kinetic "t-Butoxy(methyl)magnesium/ Dimethylmagnesium"
i-Propoxy(methyl)magnesium
n-Propoxy(methyl)magnesium
Physical Studies
Infrared Spectra
Proton Magnetic Resonance Spectra
Molecular Association Studies

TABLE OF CONTENTS (Continued)

Chapter Page

Interconversion Experiments
Pure t-Butoxy(methyl)magnesium Systems
Mixed t-Butoxy-/i-Propoxy-(methyl)magnesium Systems
Kinetic "t-Butoxy(methyl)magnesium/ Dimethylmagnesium"

III. RESULTS AND DISCUSSION 133

1,1-Diphenylethoxy(methyl)magnesium
t-Butoxy(methyl)magnesium
Preparation under Kinetic Conditions
The Cubane Form
Interconversion of the Kinetic and Cubane Forms
Interaction of Kinetic t-Butoxy(methyl)magnesium with Excess Dimethylmagnesium
i-Propoxy(methyl)magnesium
n-Propoxy(methyl)magnesium
Alkoxy(methyl)magnesium/Dimethylmagnesium Systems

IV. CONCLUSIONS 169

Thermodynamic Considerations
Kinetic Considerations

APPENDIX 1: OPERATING RANGE OF THE EBULLIOSCOPIC APPARATUS 186

APPENDIX 2: EXPERIMENTAL UNCERTAINTY IN MOLECULAR ASSOCIATION STUDIES 190

APPENDIX 3: MOLECULAR ASSOCIATION DATA 193

LITERATURE CITED 198

VITA 200

LIST OF TABLES

Table Page

PART I

THE COMPOSITION OF METHYL- AND TERTIARY-BUTYLMAGNESIUM HALIDES AND THEIR DIALKYL-MAGNESIUM ANALOGS IN DIETHYL ETHER AND TETRAHYDROFURAN AS INFERRED FROM NMR SPECTROSCOPY

1. PMR Studies of Dimethylmagnesium in Diethyl Ether 16
2. Comparison of Chemical Shift (τ) and Molecular Association (i) for Dimethylmagnesium in Diethyl Ether 20
3. Low Temperature PMR Profile of Methylmagnesium Reagents in Tetrahydrofuran 31
4. Thermodynamic Parameters for the Reaction $(t\text{-Bu})_2Mg + MgCl_2 \rightleftharpoons 2\ t\text{-BuMgCl}$ 39
5. Thermodynamic Data for the Schlenk Equilibrium $R_2Mg + MgX_2 \rightleftharpoons 2\ RMgX$ 49

PART II

THE STRUCTURE AND SOLUTION COMPOSITION OF CYCLOPENTADIENYLMETHYLMAGNESIUM IN BENZENE AND ETHER SOLVENTS

1. Comparison of Infrared Spectra of Methyl and Cyclopentadienyl Organometallic Compounds 82
2. PMR Spectra of Delocalized Cyclopentadiene Derivatives 92
3. D_2h Character Table 106

PART III

SOLUTION COMPOSITION AND INTERCONVERSION OF VARIOUS FORMS OF ALKOXY(METHYL)MAGNESIUM REAGENTS

1. PMR Chemical Shifts for Various Forms of the Alkoxy(alkyl)-magnesium Compounds in Several Solvents 157

LIST OF FIGURES

Figure Page

PART I

THE COMPOSITION OF METHYL- AND TERTIARY-BUTYLMAGNESIUM HALIDES AND THEIR DIALKYL-MAGNESIUM ANALOGS IN DIETHYL ETHER AND TETRAHYDROFURAN AS INFERRED FROM NMR SPECTROSCOPY

1. Apparatus for Preparing Grignard Reagents from Gaseous Alkyl Halides (A) Reaction Flask (B) Condenser (C) Inlet from Still (D) Alkyl Halide Inlet (E) Outlet . . . 8

2. Low Temperature Proton Magnetic Resonance Profile of Dimethylmagnesium in Diethyl Ether 14

3. Proton Magnetic Resonance Spectra of Dimethylmagnesium in Diethyl Ether at -102° Obtained by Rapid Cooling of Sample 15

4. Plot of Chemical Shift (τ) Versus Association Value (i) for Dimethylmagnesium in Diethyl Ether 19

5. Low Temperature Proton Magnetic Resonance Profile for Methyl Bromide Grignard Reagent in Diethyl Ether 27

6. Proton Magnetic Resonance Spectrum of Dimethylmagnesium in Tetrahydrofuran at -76° 32

7. Proton Magnetic Resonance Profile of Tertiary-Butyl Chloride Grignard Reagent in Diethyl Ether 35

8. Proton Magnetic Resonance Profile of Tertiary-Butyl Chloride Grignard Reagent in Tetrahydrofuran 36

9. Plot of Ln K_{eq} Versus 1/T for Tertiary-Butyl Chloride Grignard Reagent in Tetrahydrofuran 38

10. Proton Magnetic Resonance Spectra of Tertiary-Butyl Grignard Reagent in Tetrahydrofuran Containing Air Oxidation Products 41

LIST OF FIGURES (Continued)

Figure Page

PART II

THE STRUCTURE AND SOLUTION COMPOSITION OF CYCLOPENTADIENYLMETHYLMAGNESIUM IN BENZENE AND ETHER SOLVENTS

1. First Structure Proposed for Cyclopentadienylmethylmagnesium 74

2. Thermogravimetric Analysis and Differential Pressure Plot of Cyclopentadienylmethylmagnesium Monoetherate 84

3. Proposed Structure of Cyclopentadienylmethylmagnesium Monoetherate 86

4. Infrared Spectra of Cyclopentadienylmethylmagnesium Monoetherate (600-400 cm^{-1}) (A) Tetrahydrofuran Solution (B) Diethyl Ether Solution (C) Benzene Solution (D) Solid as Nujol Mull 87

5. Infrared Spectra of Coordinated and Free Diethyl Ether (A) Solid Cyclopentadienylmethylmagnesium as Nujol Mull (B) Benzene Solution of Cyclopentadienylmethylmagnesium Monoetherate (C) Benzene Solution of Diethyl Ether 90

PART III

SOLUTION COMPOSITION AND INTERCONVERSION OF VARIOUS FORMS OF ALKOXY(METHYL)MAGNESIUM REAGENTS

1. Infrared Spectra of 1,1-Diphenylethanol, A; 1,1-Diphenylethoxy(methyl)magnesium Monoetherate, B; and Desolvated 1,1-Diphenylethoxy(methyl)magnesium, C 134

2. High Frequency Infrared Spectra of Kinetic (Linear Polymer) Form of t-Butoxy(methyl)magnesium, Top; and Cubane Form of t-Butoxy(methyl)magnesium, Bottom 138

3. Low Frequency Infrared Spectra of Kinetic (Linear Polymer) Form of t-Butoxy(methyl)magnesium, Top; and Cubane Form of t-Butoxy(methyl)magnesium, Bottom 139

4. Low Temperature Proton Magnetic Resonance Spectra of the Kinetic Form of t-Butoxy(methyl)magnesium in Diethyl Ether 140

LIST OF FIGURES (Continued)

Figure — Page

5. Low Temperature Proton Magnetic Resonance Spectra of the Kinetic Form of t-Butoxy(methyl)magnesium in Tetrahydrofuran 143

6. Time Dependence of the Ambient Temperature PMR Spectra of t-Butoxy(methyl)magnesium in Diethyl Ether, Showing Signals for Kinetic Form (K) and Cubane Form (C): Spectrum A at 0 hr; Spectrum E at 386 hr 147

7. Time Dependence of the IR Spectra of t-Butoxy(methyl)-magnesium, $F_K \longrightarrow F_C$: Spectrum A at 0 hr, Spectrum E at 723 hr 148

8. PMR Spectrum of t-Butoxy(methyl)magnesium in Diethyl Ether at Ambient Temperature Showing Signals for Intermediates (X) 150

9. Time Dependence of Ambient Temperature PMR Spectra of Cubane t-Butoxy(methyl)magnesium in Tetrahydrofuran, $F_C \longrightarrow F_K$ 151

10. Low Temperature PMR Spectra of Kinetic t-Butoxy(methyl)-magnesium Plus One Mole of Dimethylmagnesium in Diethyl Ether 153

11. Infrared Spectra of i-Propoxy(methyl)magnesium, Top; and Its Decomposition Product when Heated to 105°, Bottom 156

12. Ambient Temperature PMR Spectra of t-Butoxy(methyl)-magnesium, Top; and Mixed t-Butoxy-/i-Propoxy-(methyl)-magnesium, Bottom 160

13. Infrared Spectra of n-Propoxy(methyl)magnesium, Top; and Its Decomposition Product when Heated to 130°, Bottom 162

14. Hypothetical Free Energy Profile for First Stages of Cubane to Dimer Conversion 182

15. Suggested Overall Mechanism for Dimer to Cubane Interconversion 183

16. The Effect of the Amount of Solution on the Calculated i-Value for Benzophenone Solutions in Diethyl Ether 187

SUMMARY

PART I. THE COMPOSITION OF METHYL- AND TERTIARY-BUTYLMAGNESIUM HALIDES AND THEIR DIALKYL-MAGNESIUM ANALOGS IN DIETHYL ETHER AND TETRAHYDROFURAN AS INFERRED FROM NMR SPECTROSCOPY

Variable temperature, 100 MHz nuclear magnetic resonance spectroscopy has been employed in the study of methyl- and t-butylmagnesium halides and their dialkylmagnesium analogs in diethyl ether and tetrahydrofuran. For the first time it has been possible to directly observe RMgX and R_2Mg species individually in an ether solution of these Grignard reagents. The results of these studies are entirely consistent with the earlier representation of the composition of Grignard reagents by the Schlenk equilibrium ($R_2Mg + MgX_2 \rightleftharpoons 2\ RMgX$). The results are also consistent with the view that the composition of Grignard reagents varies with the nature of the solvent, the organic group and the halide. The present results also reveal that the composition varies as well with the temperature and perhaps concentration of the solution. The solvent is the single most important factor in determining the position of the Schlenk equilibrium for alkyl Grignard reagents; the RMgX species is favored in diethyl ether and the equilibrium is approximately statistical in tetrahydrofuran. On the other hand, the rate of alkyl group exchange is primarily determined by the structure of the alkyl group and only secondarily affected by the nature of the solvent. Methyl group exchange is much faster than t-butyl group exchange under similar conditions and

alkyl groups exchange faster in diethyl ether than in tetrahydrofuran. The alkyl exchange mechanism is believed to be primarily S_Ei as observed in similar systems.

PART II. THE STRUCTURE AND SOLUTION COMPOSITION OF CYCLOPENTADIENYLMETHYLMAGNESIUM IN BENZENE AND ETHER SOLVENTS

A monoetherate of cyclopentadienylmethylmagnesium has been isolated. Comparison of its infrared spectrum in the 4000-300 cm^{-1} region with dimethylmagnesium and dicyclopentadienylmagnesium indicates that in the solid state the magnesium atoms are associated via methyl bridge bonds and that the cyclopentadienyl ring has approximately D_5h symmetry. When dissolved in benzene, the methyl bridge bonds are retained, but partial dissociation of the ether occurs. There is partial cleavage of the methyl bridge bonds when the etherate is dissolved in diethyl ether. Tetrahydrofuran cleaves the methyl bridge bonds completely. Proton magnetic resonance and molecular association studies are presented to support the above interpretation. Desolvation of the solid monoetherate is achieved readily. Unsolvated cyclopentadienylmethylmagnesium retains the methyl bridge bonds but the symmetry of the cyclopentadienyl ring is modified.

A technique using infrared spectroscopy has been developed for distinguishing between the bridging methyl system and the ordinary two-center two-electron methyl-magnesium bond.

PART III. SOLUTION COMPOSITION AND INTERCONVERSION OF VARIOUS FORMS OF ALKOXY(METHYL)MAGNESIUM REAGENTS

In these studies it has been found that not only the degree of association but also the form of association of alkoxy(methyl)magnesium reagents varies with the solvent in which they are dissolved and the steric bulk of the alkoxy group. Furthermore, the dynamic processes of exchange and interconversion between the observed forms of association are greatly affected by the steric bulk of the alkoxy group. Alkoxy-(methyl)magnesium reagents with very bulky alkoxy groups such as the 1,1-diphenylethoxy group do not appear to associate beyond the stage of a solvated, alkoxy bridged dimer. Less bulky alkoxy groups such as the t-butoxy, i-propoxy or n-propoxy groups permit the formation of linear polymers with methyl bridge bonds and cubane tetramers with μ_3 oxygen bridge bonds in solvents such as diethyl ether which are not strongly coordinating. The unsolvated cubane tetramers are quite soluble in benzene, whereas the linear polymers are not. In strongly coordinating solvents such as tetrahydrofuran, alkoxy bridged dimers predominate because the solvent cleaves methyl bridges and μ_3 oxygen bridges. Rather non-bulky alkoxy groups such as the n-propoxy group permit the formation of oligomers with 7 to 9 monomer units in very weakly coordinating solvents such as benzene. The rates and perhaps the mechanisms of the reactions by which the various forms of these reagents are interconverted and the degenerate exchange reactions within equilibrium mixtures are very dependent upon the bulk of the alkoxy group. Whereas these reactions are very rapid for compounds containing i-propoxy and n-propoxy

groups, the presence of the t-butoxy group slows down the reactions by many orders of magnitude. This phenomenon appears to be consistent with a hypothesis that most bond breaking reactions are solvent assisted and that steric bulk hinders solvent assistance in some cases to the point of requiring bond breakage without any compensating bond formation with the solvent.

PART I

THE COMPOSITION OF METHYL- AND TERTIARY-BUTYLMAGNESIUM HALIDES AND THEIR DIALKYL-MAGNESIUM ANALOGS IN DIETHYL ETHER AND TETRAHYDROFURAN AS INFERRED FROM NMR SPECTROSCOPY

CHAPTER I

INTRODUCTION

Background

The reaction of magnesium with an organic halide in the presence of a donor solvent to yield a reagent with extensive synthetic utility was recognized and developed by Victor Grignard early in this century. Since that time, there have been numerous attempts to understand, predict and control the solution composition and reactivity of these reagents. The history of this development through 1966 has been compiled into a readable review by E. C. Ashby (1) which is recommended to the reader. This introduction will concentrate mainly on relatively recent work. Even with this limitation, the great speed with which this field is advancing makes a chronological introduction very difficult. The research described in this thesis was published three years ago and it is now probably best regarded as one of the earlier works in the area of proton magnetic resonance of Grignard reagents.

When the research for this thesis was begun in 1969, it was fairly well established that the Grignard reagents could be represented in solution by what is known as the "Schlenk" (2,3) equilibrium (Equation 1).

$$R_2Mg + MgX_2 \overset{K}{\rightleftharpoons} 2\ RMgX \qquad (1)$$

Various extensions of this equilibrium have been proposed, from time to time, to account for association, ionization or other phenomena, but the simplicity of equation 1 provides a manageable starting point. An important consequence of equation 1 is that in principle it is not possible to study RMgX in solution without interference from R_2Mg. Thus, the study of Grignard reagents actually includes the study of diorganomagnesium reagents.

Although the ideal method for studying such an equilibrium would be by spectroscopic means such as IR and NMR, these methods had met with limited success. Mosher and co-workers (4) were able to estimate the value of K for methyl bromide and chloride Grignard reagents in tetrahydrofuran by infrared spectroscopy; however, the same method failed when diethyl ether was the solvent. It was not possible to distinguish diethyl ether or tetrahydrofuran solutions of ethylmagnesium bromide and diethylmagnesium by infrared analysis.

Several reports had appeared concerning NMR investigations of Grignard reagents and related dialkyl or aryl magnesium compounds in ether solvents. In 1962 Evans and Maher (5) showed that the proton resonance signal for methyl, ethyl and n-propyl Grignard reagents and the corresponding dialkylmagnesium compounds were remarkably similar and therefore concluded that the Grignard reagents in solution were mixtures of R_2Mg and MgX_2. Several years later (1966) Evans and Khan (6) succeeded in observing two species in an ether solution of pentafluorophenyl bromide Grignard reagent which they considered to be C_6F_5MgBr and $(C_6F_5)_2Mg$ in statistical equilibrium at room temperature. In 1963 Roberts and co-workers (7) had used NMR to demonstrate that inversion of

configuration at the carbon-magnesium bond of primary alkyl Grignard compounds and dialkylmagnesium compounds is rapid, but they did not study the exchange reactions or composition of these systems. House and Whitesides (8) had studied Grignard reagents and dialkylmagnesium compounds by NMR and were unable to distinguish RMgX from R_2Mg in the Grignard reagents. However, they did show by direct measurement that exchange of methyl groups between dimethylmagnesium and cyclopentadienylmagnesium is second order in methylmagnesium species and that the rate of inversion at the carbon-magnesium sigma bond of $C_5H_5MgCH_2CH_2C(CH_3)_3$ is 10^4 to 10^5 times slower than alkyl exchange.

Thus for alkyl Grignard reagents it appeared that there was little direct evidence for the composition in solution or the mechanism of alkyl exchange between R_2Mg and RMgX species. In an effort to clarify this situation we undertook the study of methyl and t-butyl Grignard reagents in both diethyl ether and tetrahydrofuran by variable temperature NMR.

Since the publication of the work contained in Part I of this thesis (9,10), there have been several important contributions. Evans and Fazakerley (11) and Ford and Grutzner (12) have studied a number of Grignard reagents by ^1H and ^{13}C magnetic resonance and have obtained data on the position of the Schlenk equilibrium at low temperatures. Grutzner and co-workers (13), like Zieger and Roberts (14) several years earlier, examined the 1,3-shift of allyl Grignard reagents. Fraenkel and co-workers (15) extended work by other groups (7,8) on the mechanism of inversion at the carbon magnesium bond.

Purpose

The purpose of the research described in Part I of this thesis is to examine factors affecting the position and dynamics of the Schlenk equilibrium. Some of these factors are solvent polarity, alkyl group structure, halide electronegativity and concentration of the reagent solution. It is intended to draw together the results of the proton magnetic resonance (PMR) studies described in Chapter III and previous literature results into a detailed discussion of the Schlenk equilibrium in Chapter IV so that a useful theory can be developed to predict the solution behavior of any particular Grignard system on the basis of a relatively few basic principles.

CHAPTER II

EXPERIMENTAL

General Considerations

All organomagnesium reagents react rapidly with oxygen and moisture, thus extreme care was taken to avoid exposure of these compounds to air. Most of the techniques used are described by Shriver (16) and the dry box system employed in this work has recently been discussed (17). Since organomagnesium reagents do not attack ether solvent and since extreme care was taken in all manipulations, it was frequently only necessary to check the composition of a reagent solution by hydrolyzing an aliquot and analyzing for magnesium by volumetric analysis using the disodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA) as a standard (18). Volhard titration (19) for halogen and/or acid titration for total base in a hydrolyzed sample was occasionally used as a check. Most of the samples used in the studies described below were prepared by standard techniques. Typical reactions are described in the following paragraphs, but in general there is no difficulty in scaling the reactions up or down within reasonable limits. Minor variations of equipment or techniques also cause no problems as long as exclusion of air is considered.

Solvents

Bulk reagent solvents were pre-dried over sodium wire then stored in two-liter stills over the appropriate metal hydride (diethyl ether

over $LiAlH_4$ and tetrahydrofuran over $NaAlH_4$). When desired, the solvents were distilled into round bottom storage flasks for use in the dry box or distilled directly into addition funnels or reaction flasks when possible.

Grignard Reagents

The method used to prepare Grignard reagents was dictated by the physical properties of the alkyl halides: methyl chloride and bromide are gases under ordinary conditions while methyl iodide and tertiary butyl halides are liquids.

For the gaseous alkyl halides the apparatus shown in Figure 1 was employed. After charging the reaction flask with the desired amount of magnesium, the apparatus was flamed in vacuo. Once cooled, the condenser was filled with dry ice and acetone. Solvent was distilled in and the methyl halide was passed over NaOH pellets and molecular sieve into the reaction vessel. The amount of alkyl halide was controlled to determine whether excess magnesium or excess alkyl halide was used. The total amount of solvent was controlled to obtain the desired concentration range.

When a liquid alkyl halide was employed, it was added to the magnesium from a dropping funnel as a concentrated solution in the desired solvent. Subsequently, extra solvent was added to achieve the desired concentration.

Dimethylmagnesium

Dimethylmagnesium was prepared from neat dimethylmercury and 100% excess magnesium by reacting for 18 to 24 hrs at room temperature.

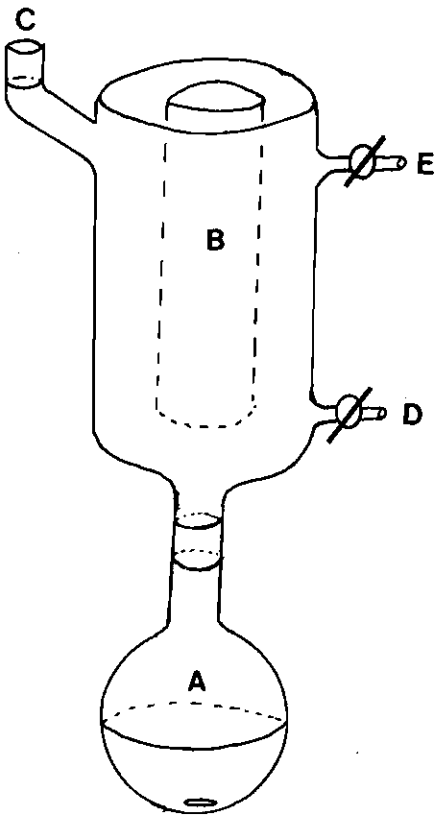


Figure 1. Apparatus for Preparing Grignard Reagents from Gaseous Alkyl Halides (A) Reaction Flask (B) Condenser (C) Inlet from Still Head (D) Alkyl Halide Inlet (E) Outlet

The product was extracted from the amalgam with the desired solvent and filtered when necessary. In the course of the work it was found that pre-dried Celite (20) filter-aid greatly improved filtration of all organomagnesium reagent solutions.

Magnesium Halides

Solutions of magnesium halides were prepared by reaction of the mercuric halide of choice with 100% excess magnesium in the desired solvent. The product was isolated by filtration or decantation from the amalgam.

Sample Preparation

For samples which were intended for repeated or extended study, the following technique was used. The material to be studied was taken into the dry box and a sample was injected by syringe into an NMR tube which had been fitted with a thick walled adaptor for sealing. Tetramethylsilane was added and a three-ring cap used for a temporary seal. Silicon grease was applied around the bottom of the cap before removing the tube from the dry box, freezing in liquid nitrogen and sealing with a torch. For temporary samples, standard NMR tubes were used and they were sealed only by a three-ring cap. These samples were stored in the dry box and run within 24 hrs of their preparation.

Nuclear Magnetic Resonance (NMR) Technique

Spectra were made on a Jelco 100 MHz spectrometer using the standard variable temperature unit. This unit had been calibrated upon installation and was checked by connecting a digital volt meter

across the thermocouple leads and comparing the observed voltages at various temperature settings to those expected from the thermocouple. The accuracy of the temperature readings is estimated to be ±4° with a precision of ±2° at the extremes of the controlled range.

Temperature equilibration in the NMR samples was determined by monitoring the signal feedback meter (Jelco's S-meter) which is very sensitive to changes in the gross dielectric properties of the sample which change with solvent and temperature, concentration, etc. Stabilization of the S-meter in the null position was taken as the indication of temperature equilibration within the sample. For the determination of chemical shifts in connection with the Schlenk equilibrium study, the digital output of the spin-decoupler unit was used with an estimated accuracy of 0.1 cps. For other experiments, pre-calibrated chart paper was used.

Computer Simulation of Spectra

The DNMR program for simulation of complex exchange-broadened nuclear magnetic resonance spectra was written by Binsch and Kleier (21). The program was obtained through the services of the Quantum Chemistry Program Exchange (QCPE) at Indiana University in Bloomington, Indiana. The program has been slightly revised by its authors since its use in this work. The original version will be described here. The program is written in FORTRAN IV for a UNIVAC 1108 computer equipped with a CALCOMP plotter. A complete description of the program and input parameters was provided with the program.

It proved convenient to modify the output of the program very

slightly for use with this research. In the original program the subroutine SPECT which constructs the CALCOMP plot was set up so that successive plots were drawn on top of one another. In the original program, each time the subroutine PLOT was called, the X and Y coordinates were set to zero (0,0) in the statement

```
CALL PLØT (0,0,-3)
```

This statement was replaced by two statements,

```
XGØ = XMAX + 0.1 * XMAX

CALL PLØT (XGØ,0,-3)
```

which have the combined effect of advancing the plotter to a new origin (XGØ,0) when initiating a new plot rather than returning to the original origin (0,0). The integer variable "-3" in the call list is a carriage control device which causes the pen to be raised while moving to the new origin.

Computation was carried out at the Rich Electronic Computer Center at the Georgia Institute of Technology.

The problem to which the computation was applied was the determination of the populations of tert-butyl groups in two magnetically nonequivalent sites (RMgX and R_2Mg) and estimation of the rate of chemical exchange of the tert-butyl groups between these sites by comparing spectra generated by the CALCOMP plotter with experimental spectra. Inspection of the experimental spectra revealed that the temperature dependent line broadening due to chemical exchange was on the same order

of magnitude as errors inherent in visually comparing the experimental and computed spectra. Thus, while it was possible to estimate the order of magnitude of the pre-exchange lifetime of tert-butyl groups, it was not feasible to try to calculate activation parameters for exchange. An example of the input data used to generate a spectrum is found in Appendix 1.

CHAPTER III

RESULTS

Dimethylmagnesium in Diethyl Ether

The low temperature proton magnetic resonance behavior of solutions of dimethylmagnesium in diethyl ether is presented in Figures 2 and 3 and the corresponding numerical results are listed in Table 1. Spectra of a 0.31 M solution were recorded successively at intervals of 10 to 20 minutes as the sample was cooled and thermal equilibrium was achieved. The important observations are that the signal for the methyl protons shifts to higher field and broadens while a small signal at approximately 11.32_{τ} is resolved. At very low temperatures the high field signal reaches a limiting chemical shift at 11.72_{τ} and resolves into two peaks at 11.69_{τ} and 11.74_{τ} which overlap to a large extent. Several small generally broad signals are also detected between 11.00_{τ} and 11.35_{τ}. These small signals and the signal at 11.69_{τ} lose intensity relative to the 11.70_{τ} signal with time. To enhance the intensity of these signals, the sample was warmed to room temperature and allowed to redissolve (a large amount of white solid formed below -30°). Then the sample was frozen into a solid solution (no precipitate) by dipping in liquid nitrogen for several seconds. The sample was warmed slightly until partial melting occurred and inserted directly into the NMR probe which was pre-cooled and tuned at -102°C. The spectrum which was obtained showed enhanced signal amplitude, particularly of the signals in

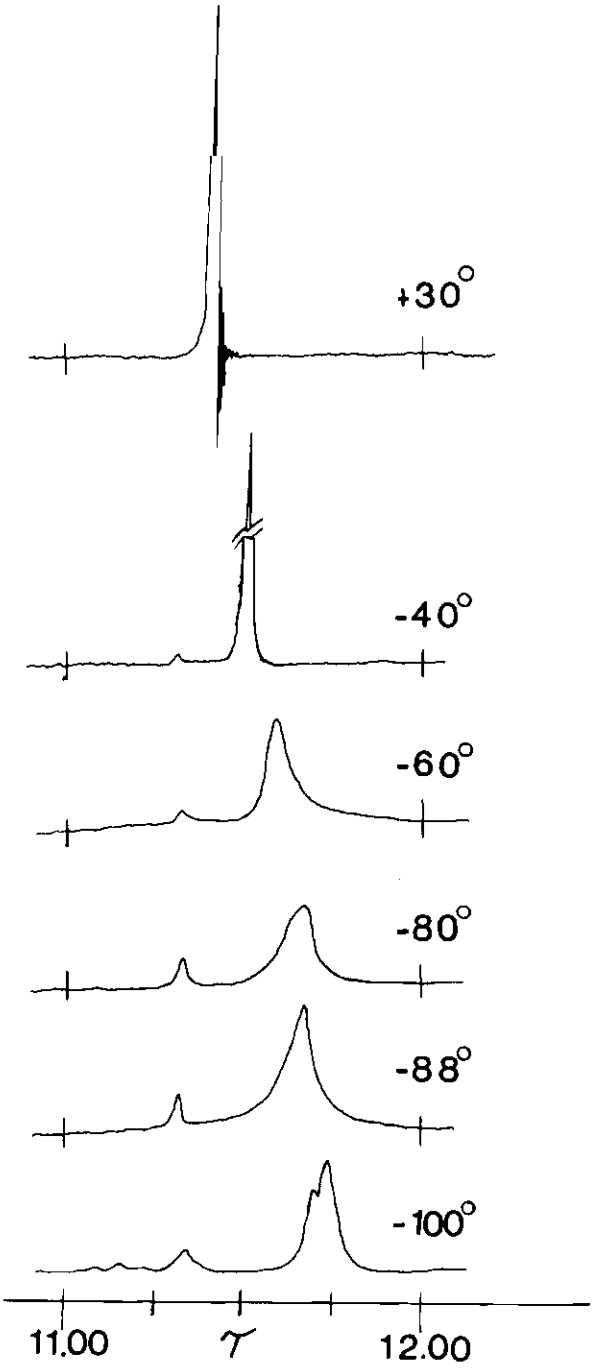


Figure 2. Low Temperature Proton Magnetic Resonance Profile of Dimethylmagnesium in Diethyl Ether

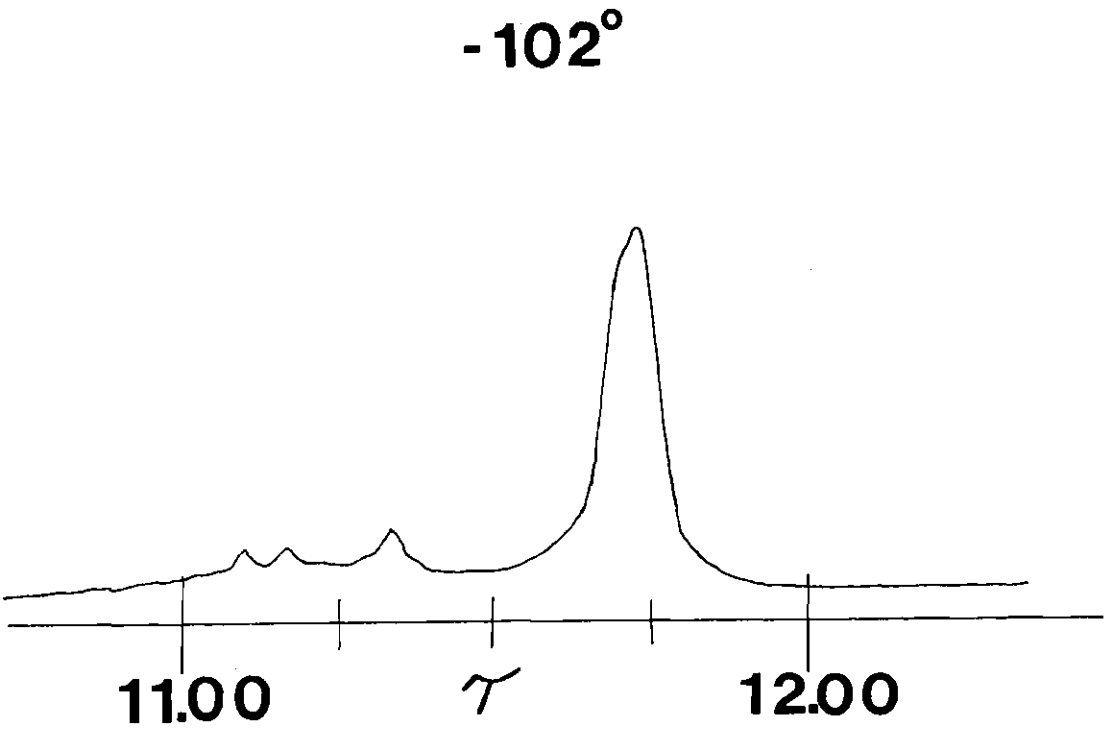


Figure 3. Proton Magnetic Resonance Spectra of Dimethylmagnesium in Diethyl Ether at -102° Obtained by Rapid Cooling of Sample

Table 1. PMR Studies of Dimethylmagnesium in Diethyl Ether

Concentration (Molar)	Temperature (°C)	Chemical Shift[b] (in Hz upfield from TMS)
Part A: Previous Results (8)[a]		
0.71	~ 30	139
0.18	~ 30	142
0.090	~ 30	145
0.028	~ 30	150
0.84	+ 33	140
0.84	- 29	145
< 0.84	- 54	147 (3.6)
Part B: Present Study[c]		
	Sequential Cooling	
0.31	+ 30	145 (1.5)
	- 12	147 (1.5)
	- 20	149 (1.5)
	- 30	138 (-), 150 (1.5)
	- 40	138 (-), 151 (3)
	- 60	132 (3), 159 (5)
	- 80	132 (2), 167 (10)[d]
	- 88	132 (2), 169 (8)[d]
	-100	132 (3), 170 (5)[e], 174 (5)[e]
	-105	132 (4), 169 (4)[e], 174 (4)[e]
	-110	132 (3), 169 (4)[e], 174 (4)[e]
	Rapid Cooling	
	-102	110[f], 116[f], 133[f], 170(sh),174

[a] Converted comparable 100 MH_z shifts

[b] Full widths at half-height ($W_{1/2}$) are given in parentheses

[c] This work

[d] Signal is distinctly asymmetric

[e] Assuming each component is symmetric

[f] These signals rest on a distinct rise in the base line between $\sim 11.00\tau$ and $\sim 11.50\tau$ which is as intense as the signals

the 11.00 to 11.40τ region and at 11.69τ.

Without relying on any structural arguments, the large shift in the position of the major high field signal(s) upon cooling (11.45τ $\longrightarrow$ 11.69τ, 11.74τ) is too large to be accounted for by changes in overall characteristics of the solvent, and can be interpreted in terms of either specific solvation effects or changes in the composition of an exchange system. Before discussing these results in detail it is helpful to review the data already available on the composition of dimethylmagnesium.

In the solid state, dimethylmagnesium exists as a linear polymer in which the magnesium atoms are four coordinate by virtue of the formation of electron deficient methyl bridge bonds (22). Dissolution of dimethylmagnesium in diethyl ether is an endothermic process and solvent free dimethylmagnesium can be readily obtained from diethyl ether by evaporating the solvent at room temperature (23). Molecular association studies in boiling diethyl ether have revealed that the degree of association as measured by the i-value varies from 1.8 near saturation (about 0.8 m) to 1.0 at high dilution (24). Proton magnetic resonance studies (5) show that the exchange-averaged methyl proton chemical shift varies from about 11.40τ to 11.60τ over the same concentration range. The change in chemical shift can be attributed to two main effects: First, changes in the composition of the exchange system and second, solvent anisotropy. The effect of solvent anisotropy is generally small (less than 0.1 ppm) and the shifts are linearly related to concentration (and temperature). A small, linear shift was observed for methyl iodide Grignard reagent in diethyl ether as a function of concentration (5),

but the plot of chemical shift versus concentration for dimethylmagnesium in diethyl ether was not only found to be much larger but also definitely not linear*. Thus, the observed variation of chemical shift must primarily reflect changes in association of dimethylmagnesium.

It is interesting to plot the PMR results for dimethylmagnesium in diethyl ether versus the molecular association results as in Figure 4. The data from which this plot was drawn is found in Table 2. There is good correlation of the two types of measurements. However, due to the previously mentioned effect of solvent anisotropy, extrapolation of the plot in Figure 4 to i-values of 1.0 and 2.0 does not give highly accurate predictions of the chemical shifts of monomer/terminal methyl groups and bridging methyl groups. Nonetheless, if these interfering effects are ignored, the chemical shift of monomeric dimethylmagnesium where the methyl group is bound to magnesium by a two-center two-electron bond should be about 11.60τ and the chemical shift for a methyl group in the terminal site of a polymer should be about the same since the bonding is similar. At an i-value of 2.0, the ratio of bridging to terminal methyl sites in any sort of equilibrium involving only the linear polymers must be 1:1. For example, if the i-value of 2.0 reflects only a dimer in solution, then the bridging to terminal ratio is 2:2. If the i-value is 2.0 and the equilibrium is trimer $\rightleftharpoons$ monomer,

*The magnetic field experienced by a solute molecule will depend in part on the bulk magnetic susceptability of the solution. The average orientation of molecules in the bulk solvent surrounding a solute molecule is temperature and concentration dependent and as this average orientation changes, so will the chemical shift. These effects are usually small compared to specific solvation effects but may amount to a tenth of a part per million (ppm) in chemical shift or more in specific cases.

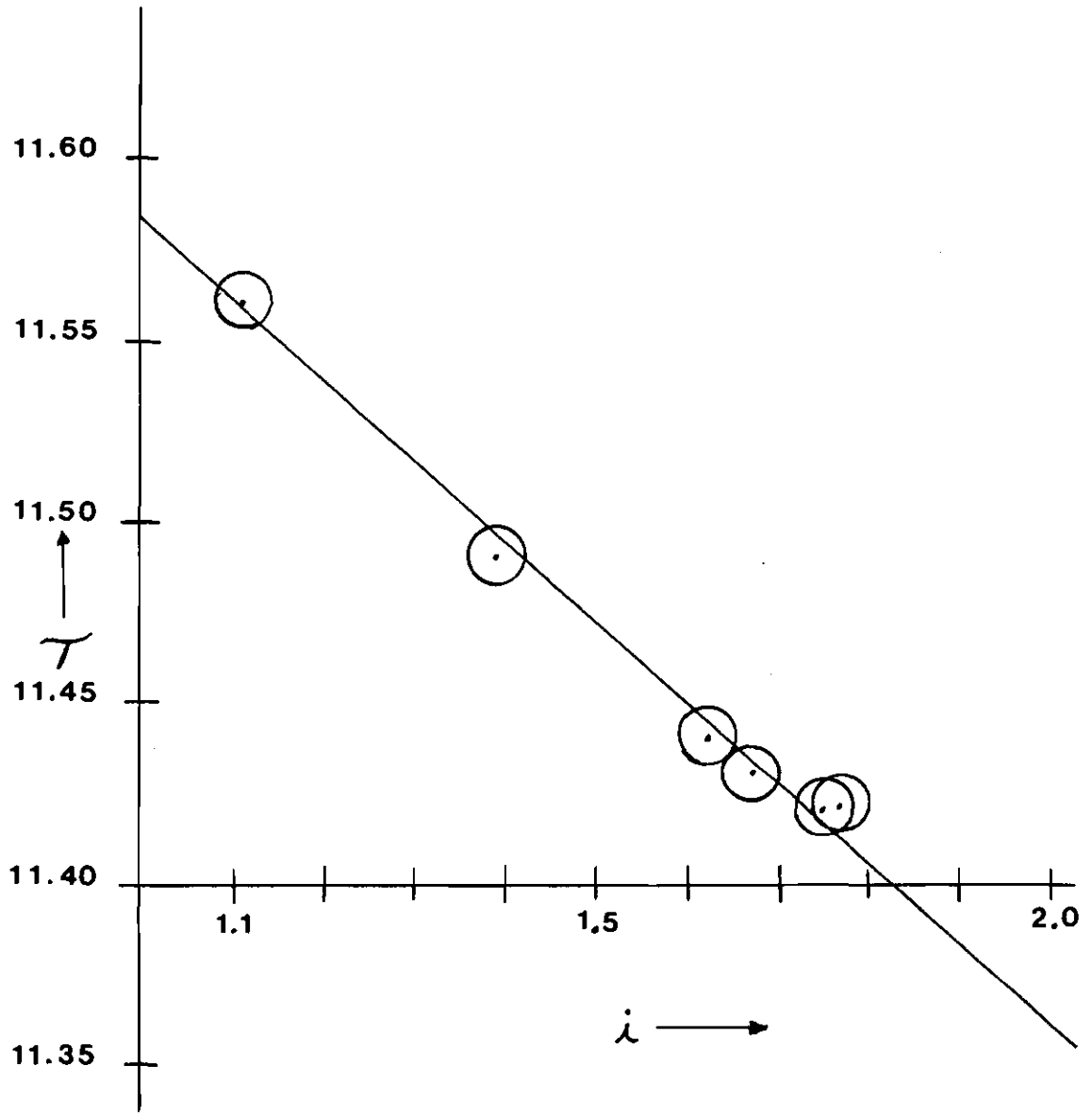


Figure 4. Plot of Chemical Shift (τ) Versus Association Value (i) for Dimethylmagnesium in Diethyl Ether

Table 2. Comparison of Chemical Shift (τ) and Molecular Association (i) for Dimethylmagnesium in Diethyl Ether

Molality[a]	i-value[a]	Chemical Shift (τ)[b]	$(CH_3)_2Mg/Et_2O$[b]
0.024	1.11	11.56	0.002
0.087	1.39	11.49	0.006
0.275	1.62	11.44	0.020
0.358	1.67	11.43	0.026
0.499	1.75	11.42	0.037
0.607	1.76	11.42	0.045

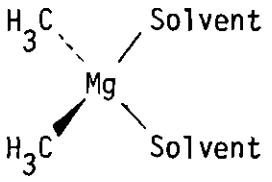
[a]From Reference 24

[b]Comparable values taken from the curve in Reference 5

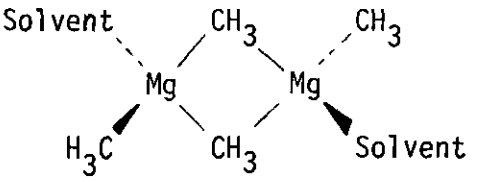
then for every trimer there must be one monomer and the bridging to terminal plus monomer ratio is 4:2+2. Similar reasoning leads to the conclusion that for equilibria involving only linear polymers of the type found for solid dimethylmagnesium, an i-value of 2.0 requires equal numbers of bridging and terminal plus monomer methyls. Using the weighted average law (Equations 1 and 2 in Appendix 2), assuming a terminal (monomer) chemical shift of 11.60τ and taking the extrapolated 2.0 i-value chemical shift of the equilibrium mixture (11.36τ) as the exchange averaged signal require a bridging methyl chemical shift of 11.12τ. This result is qualitatively similar to that observed in other organometallic systems (e.g., dimethylberyllium (25) or trimethylaluminum (26)) in that the terminal and monomer methyl chemical shifts occur at high field while the bridging methyl chemical shifts occur at low field.

Returning to the observed spectra, Figures 2 and 3, structural features of the components of the dimethylmagnesium system may be inferred from the low temperature PMR spectra. In accordance with the semi-quantitative predictions based upon the chemical shift versus i-value plot, signals at 11.74 and 11.70τ are resolved from signals at 11.10, 11.16 and 11.33τ at -102°. The high field signals are attributable to terminal and monomer methyl sites while the low field signals are attributable to bridging methyl sites. In addition, since the bridging methyl signals and the 11.70τ signal decrease in intensity with time relative to the 11.74τ signal, the 11.70τ signal is assigned to terminal methyl sites in polymers (T) and the 11.74τ signal is assigned to methyl groups in monomeric dimethylmagnesium (M). Finally, if it is

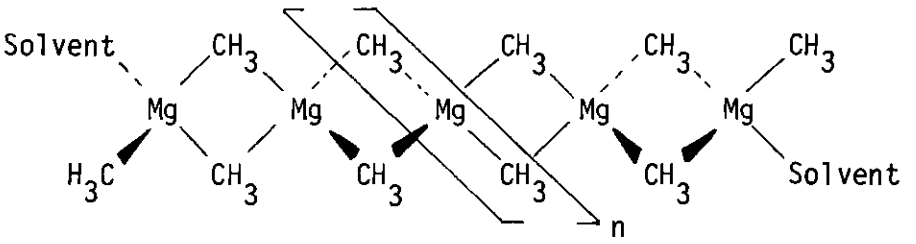
argued that an "internal" bridging methyl site (b_3) should be more electron deficient and hence more deshielded than an "external" bridging methyl site (b_2), the several signals in the bridging methyl region can be explained and assigned by a system similar to that developed by Kovar and Morgan (25) to explain the PMR spectrum of dimethylberyllium in dimethyl sulfide*.



M



T b_1 T



T b_2 b_3 b_3 b_2 T

$$\tau_{b_3} < \tau_{b_2} < \tau_{b_1} << \tau_T \lesssim \tau_M$$

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*The assignments in the dimethylberyllium/dimethyl sulfide system as given by Kovar and Morgan are

$$\tau_{b_3} = 10.31, \quad \tau_{b_2} = 10.41, \quad \tau_T = 10.80,$$

τ_M (monosolvate) = 10.77 and τ_M (disolvate) = 11.30

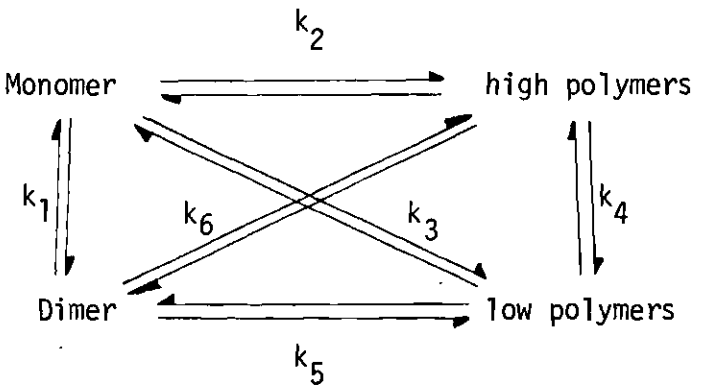
with τ_{b_1} unobserved.

While this system of assignments seems to work rather well, it should probably be considered tentative since the shielding (chemical shift) arguments cannot be backed up with arguments based on the relative intensities of the signals. For example, in the dimethylberyllium/dimethyl sulfide system, Kovar and Morgan were able to integrate the intensities of the terminal (T) and bridging signals (b_2) because they were sufficiently resolved from monomer (m) and other bridging signals (b_1, b_3) and they were thus able to argue that a trimer with a bridging methyl (b_2) to terminal methyl (T) ratio of 4:2 was the most abundant polymer in solution at intermediate temperatures. In the dimethylmagnesium/diethyl ether system, the near coincidence of the signal for terminal methyl groups (T) and monomer methyl groups (M) precludes such arguments.

Now that the types of chemical structures present in solution have been deduced from the low temperature spectrum, it is worthwhile to look at the changes in the PMR spectrum with temperature. Between +30° and -40° the main signal shifted from 11.45τ to 11.51τ and a small signal was resolved at lower field (11.38τ)*. When -88° was reached the low

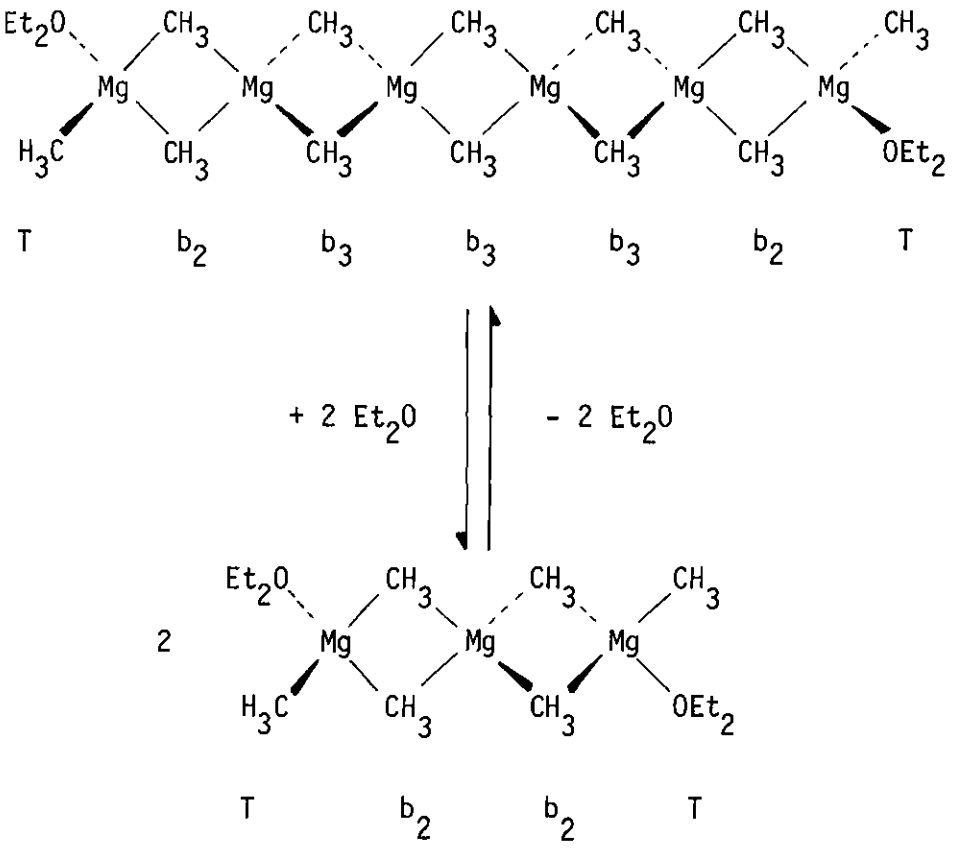
*Dimethylmagnesium in ether has been observed in this temperature region before (8), but no signal at 11.32τ was reported. We, therefore, questioned the origin of this signal with regard to alkoxide impurities which were reported to produce signals in this region. Two experiments were directed toward this problem. A completely new sample of dimethylmagnesium was prepared in a dry box under a stream of prepurified nitrogen. Air and moisture were rigorously excluded. A PMR sample was prepared as described in the experimental section. This sample showed the same 11.32τ signal with no loss of relative intensity (sample concentration 0.81 M). In a second test, an ether solution of methanol was added to $(CH_3)_2Mg$ in the same solvent in a mole ratio of 1:2. A large amount of solid formed. Methoxy groups could not be detected in the NMR spectrum of the supernatant liquid. Their signals might be hidden by the ether signals. When the supernatant liquid was observed at low temperature, the signal for methyl bound to magnesium rapidly deteriorated at -41°C and disappeared with only one signal (at 11.50τ) even being observed.

field signal had sharpened and shifted to 11.32τ while the high field signal was still asymmetric, broad and centered at 11.69τ . The area ratio of these two signals was roughly 1:10. At -100° several new low field signals were resolved and the high field signal was resolved into a main peak at 11.74 with a shoulder at 11.69τ. The area ratio of all the low field signals to the high field signals was roughly 1:5. A general exchange model which is consistent with this behavior can be suggested as below:



with $k_4 \gg k_2 > k_3 > k_5 \cong k_6 \gg k_1$. This scheme accounts for the resolution of the bridging methyl signal of the dimer (b_1) while exchange between terminal (T) and bridging sites in higher polymers (b_2, b_3) is still fast. The reason for such a situation can be attributed to greater electron deficiency at the methyl bridges near the center of the high polymers which enhances nucleophilic attack by solvent resulting in cleavage of the bonds and exchange of bridging sites (b_2 and b_3) with terminal sites (T). Notice that in the reaction below there is exchange between b_3 and T sites and between b_2 and b_3 sites. The important feature of this exchange mechanism is that exchange of the internal bridging

methyls (b_3) with terminal methyls (T) does not need to involve intramolecular migration of the methyl groups along the chain through b_2 sites to terminal sites.



Although it has not been necessary to invoke a monosolvate-disolvate equilibrium to explain the above results, such a situation was shown to exist in the case of monomeric dimethylberyllium in dimethyl sulfide (25) and could conceivably be invoked in the magnesium system to account for part of the observed low temperature chemical shift. However, the larger radius of magnesium (1.36 Å) compared to beryllium (1.04 Å), as estimated from the metal-metal distances in the $(CH_3)_2M$ (M = Be or Mg) polymers, suggest that a distinct monosolvate is not as

likely in the magnesium system.

Methyl Grignard Reagents in Diethyl Ether

The results of low temperature PMR spectroscopy on solutions of a methyl bromide Grignard reagent in diethyl ether is given in Figure 5. At -100° two signals are observed. The high field signal is at approximately 11.70$_\tau$ where terminal and monomer methyl sites in dimethylmagnesium have been shown to resonate and thus this signal is attributed to dimethylmagnesium. The low field signal, which is not greatly shifted from the position of the room temperature signal of the Grignard solution, is at 11.55$_\tau$ and the only logical assignment of this signal is to a solvated and perhaps associated (by halogen bridges) form of methylmagnesium bromide.

The spectra obtained at -100° or below showed time dependence. The signal for methylmagnesium bromide decreased with time relative to the signal for dimethylmagnesium and increasing the temperature from -105° to -90° did not reverse the trend. In addition, it was found that when a 0.3 M methyl bromide Grignard solution in diethyl ether was cooled to -70° for 10 min followed by filtration and analysis of the precipitate, the ratio of total magnesium to basic magnesium in the solid phase was 1.00:0.86 similar to previous crystallization results (27). Obviously, at low temperatures methylmagnesium bromide disproportionates to dimethylmagnesium and sparingly soluble magnesium bromide. It is not possible to determine meaningful equilibrium constants for the Schlenk equilibrium under these conditions and any attempt to calculate enthalpy and entropy changes from this data would be even more

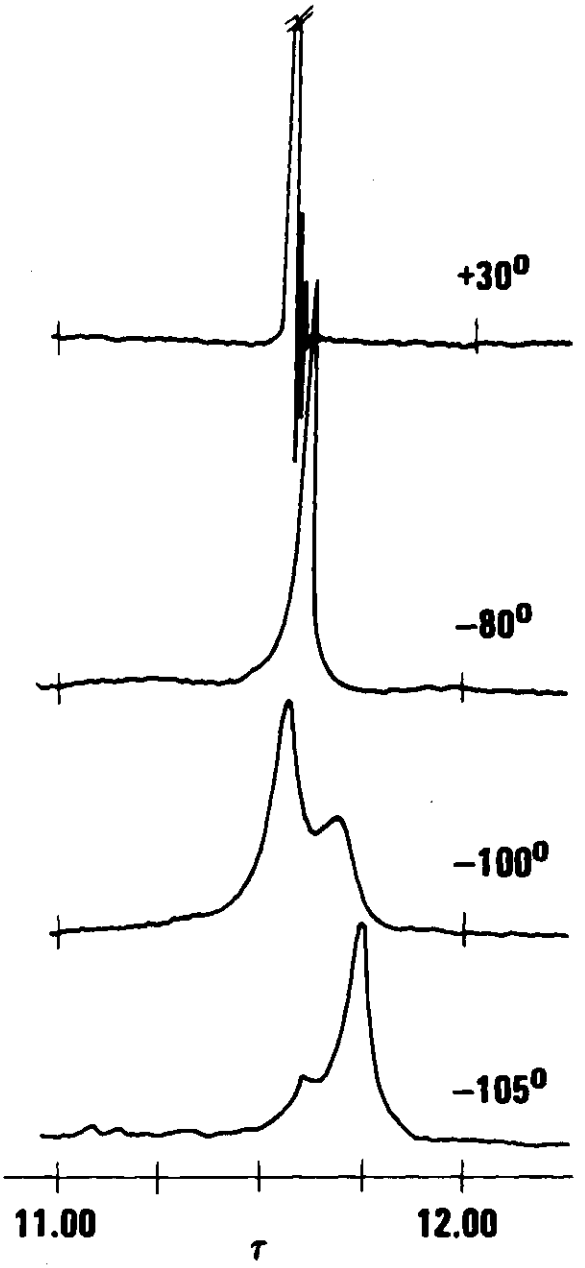


Figure 5. Low Temperature Proton Magnetic Resonance Profile for Methyl Bromide Grignard Reagent in Diethyl Ether

meaningless since depending upon the chronological order in which spectra at different temperatures were made, the calculated enthalpy and entropy changes could be positive, negative or zero. This point is made because other workers (11,12) have reported such measurements under similar conditions. In one case (12), the spectra were run by a technician who can be presumed to have been unfamiliar with the possible importance of such observations as precipitation of the sample at low temperature and in both cases it is implied that undisturbed solutions were examined though any other possibility was ignored. Thus, while there is no direct evidence that the results of others (11,12) have been prejudiced by inadequate experimental control, a circumstantial case can be brought up in favor of rechecking these reports.

In spite of the previous arguments, some thermodynamic data can be gleaned from the temperature dependence of the methyl bromide Grignard reagent spectrum. The spectra at low temperature indicate that dimethylmagnesium arises in the system as the result of precipitation of magnesium bromide and the Schlenk equilibrium must lie well in favor of methylmagnesium bromide at room temperature. (I.e., $k_{eq} > 10^2$). If the enthalpy of the Schlenk equilibrium for the forward reaction were positive (i.e., endothermal),

$$R_2Mg + MgX_2 \rightleftharpoons 2\ RMgX \quad ,$$

the large temperature change in going from +30° to -80° would be expected to cause the equilibrium to shift well in favor of the $(CH_3)_2Mg$ species with a corresponding shift in the spectrum. However, the results suggest that any shift of the observed average exchange

signal toward 11.74τ from 11.55τ is due to precipitation. Thus, lowering the temperature probably drives the solution equilibrium to the right (towards CH_3MgBr) implying a negative (exothermal) enthalpy for the forward reaction. This result is consistent with the thermochemical measurements on a similar system by Smith and Becker (28,29). They determined the enthalpy for the redistribution of diethylmagnesium with magnesium bromide to be -3.7 kcal/mole at room temperature. Thermodynamic aspects of the Schlenk equilibrium will be discussed in detail after the results on tetrahydrofuran solutions are presented.

The study of this system was expanded in two experiments. First, a 1:1 mixture of dimethylmagnesium and methyl bromide Grignard reagent was observed under the same conditions as the pure Grignard reagent. The results were that the signals characteristic of dimethylmagnesium were more predominant at all temperatures. In the last experiment, "synthetic" methyl bromide Grignard and 1:1 methyl bromide Grignard-dimethylmagnesium were prepared by mixing solutions of dimethylmagnesium and magnesium bromide in 1:1 and 2:1 ratios respectively. The spectra of these mixtures were in every way consistent with those of the "authentic" methyl bromide Grignard and 1:1 Grignard-dimethylmagnesium mixture.

To complete the survey of methyl Grignard reagents in diethyl ether, a solution of methyl iodide Grignard (∿0.5 M) was observed at temperatures between +20° and -40°. Attempts to obtain data at lower temperatures were inhibited by virtually total precipitation of the reagent. At room temperature, a single signal was observed at 11.49τ. At -41° the main signal was at 11.51τ with two very small signals at 11.28τ and

11.34τ. The low field signals are probably due to bridging methyl sites. The high field signal is an average exchange signal for RMgX and R_2Mg. Methyl chloride Grignard reagent is known to disproportionate in ether solution at room temperature depositing magnesium chloride. Thus, it was not studied.

Dimethylmagnesium in Tetrahydrofuran

Dimethylmagnesium appears to be monomeric over a wide concentration range in tetrahydrofuran (24). The results of low temperature proton magnetic resonance studies on the dimethylmagnesium/tetrahydrofuran system are given in Table 3 and Figure 6. There are several points which should be noted. The effect of temperature lowering on the chemical shift of the methyl signal (11.76τ→11.83τ) was relatively small compared to the change in chemical shift observed for the methyl signal in diethyl ether (11.45τ→11.69, 11.74τ). This small shift is probably due almost entirely to the previously mentioned effect of temperature dependent solvent anisotropy, as opposed to any major change in the composition of an exchange system. At -76° the major signal at 11.83τ is attributed to $(CH_3)_2Mg$ monomer and a small signal at 11.70τ is attributed to terminal sites in an associated species. The low signal to noise ratio partially obscures the bridging signal which is broad and centered near 11.50τ.

Methyl Grignard Reagents in Tetrahydrofuran

The methyl bromide and methyl chloride Grignard reagents in tetrahydrofuran have been revealed by infrared spectroscopy (4) to be essentially statistical mixtures of solvated magnesium halide,

Table 3. Low Temperature PMR Profile of Methylmagnesium Reagents in Tetrahydrofuran

Temperature (°C)	Chemical Shift (τ)		
	$(CH_3)_2Mg$	CH_3MgBr	CH_3MgCl
+ 20	11.76	11.70	11.72
- 20		11.77	
- 40		11.78	11.77
- 60	11.81	11.80	
- 76	11.50, 11.70, 11.83		
- 90		11.84	11.82
- 100		11.85	11.83

These are convenient comparison temperatures. The chemical shifts cited are for the observed temperature ± 3° of that listed.

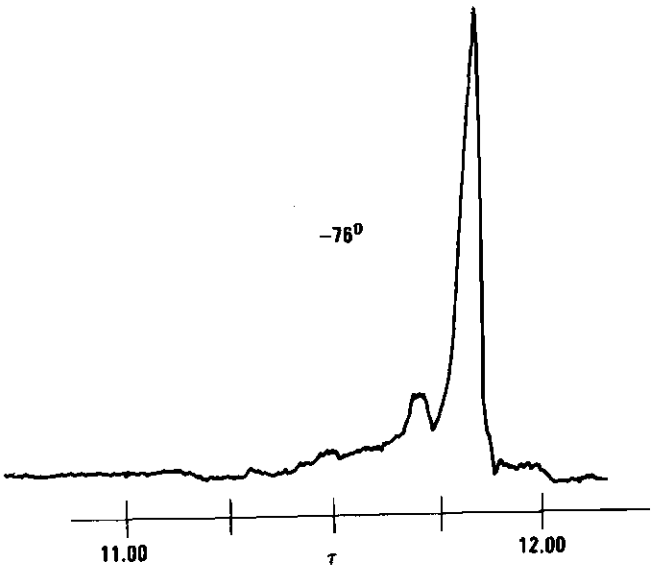


Figure 6. Proton Magnetic Resonance Spectrum of Dimethylmagnesium in Tetrahydrofuran at -76°

dimethylmagnesium and methylmagnesium halide at room temperature (e.g., $k_{eq} \cong 4$). Calorimetric measurements indicate that the forward reaction in the Schlenk equilibrium for similar Grignard reagents in tetrahydrofuran is endothermic (30). Thus, lowering the temperature should favor shifting the equilibrium in favor of solvated MgX_2 and R_2Mg. As shown in Table 3, the chemical shift of the proton magnetic resonance signal for methyl bromide and methyl chloride Grignard reagents in tetrahydrofuran is greatly temperature dependent, shifting steadily to higher field at lower temperatures. Using the sequential cooling technique which requires on the order of 15 to 30 minutes for each spectrum to be obtained (e.g., one or two hours to obtain a full sequence of spectra), separate signals for $(CH_3)_2Mg$ and CH_3MgBr or CH_3MgCl were never observed. Apparently by the time temperatures low enough for slow exchange conditions to be met were reached, the equilibrium had shifted almost entirely in favor of $(CH_3)_2Mg$ and $MgBr_2$ or $MgCl_2$ solvates. It is interesting that Evans and Fazakerley (11) were in fact successful in observing separate signals for CH_3MgBr and $(CH_3)_2Mg$ solvates in tetrahydrofuran at -80°. It is likely that they achieved this result by rapidly cooling the sample and obtaining the spectrum before equilibrium was achieved. Here again, integration of the signals does not give a true value of the equilibrium constant for the Schlenk equilibrium since true equilibrium has not been achieved. In addition, a sample of 0.68 M methyl bromide Grignard reagent in tetrahydrofuran was cooled to -70° for 20 minutes. Analysis of the solid phase showed the Mg:Br ratio to be 1.0:1.2, while the liquid phase ratio of magnesium to bromide was found to be 1.0:0.44 indicating that halogen rich species were

precipitated under the conditions of the proton magnetic resonance experiment. From these data, it can be calculated that approximately 75% of the magnesium in the sample was in the solid phase.

In spite of the uncertainties apparent in the use of low temperature observation to quantitatively measure the position of the Schlenk equilibrium, reasonable estimates of the position of the Schlenk equilibrium at room temperature were made by applying the weighted average law for rapidly exchanging systems to the assumption that the chemical shifts of dimethylmagnesium and methylmagnesium halide solvates in the absence of exchange are 11.76 and 11.64τ respectively. The chemical shift for the methylmagnesium halide solvates was estimated by observing samples containing large excesses of halide. Details of the calculations are contained in Appendix 2. The resulting equilibrium constants were 4 $\pm$ 2.6 for methyl bromide Grignard and 1 $\pm$ 0.72 for methyl chloride Grignard in tetrahydrofuran at room temperature in agreement with previous results (4,30).

Tertiary-Butylmagnesium Compounds in Diethyl Ether and Tetrahydrofuran

The only prior art in the area of tertiary-butylmagnesium compounds is a report by Coates and Heslop (31) of a bis(tetrahydrofuranate) complex of di-t-butylmagnesium and a bis(diethyl etherate) of t-butylmagnesium chloride dimer. When dissolved in benzene the latter compound exhibited a single t-butyl signal at ca. 8.75τ.

Examination of t-butyl chloride Grignard reagent in diethyl ether and tetrahydrofuran by variable temperature proton magnetic resonance gave the results shown in Figures 7 and 8 respectively. At +30° in

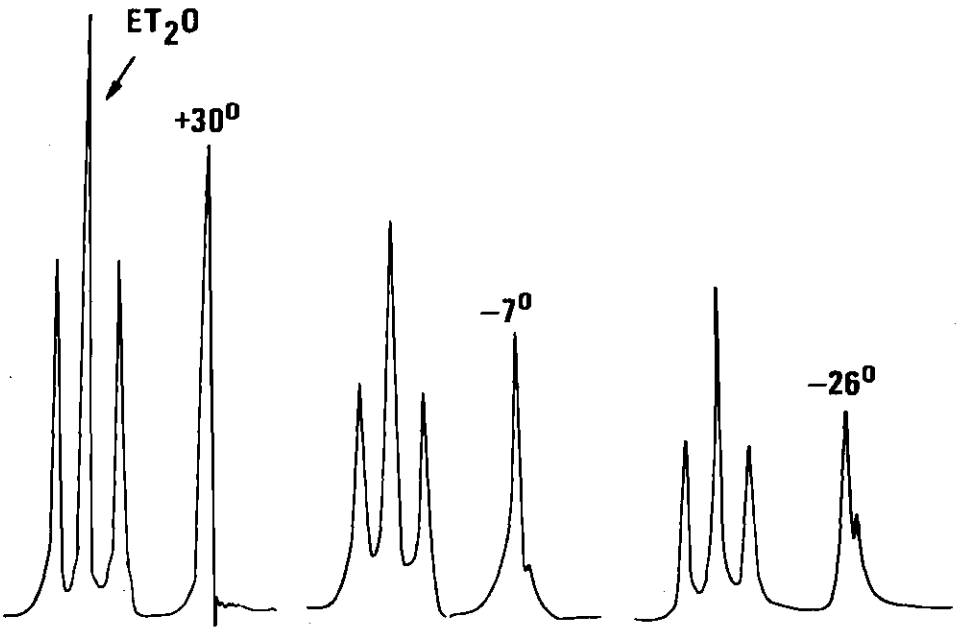


Figure 7. Proton Magnetic Resonance Profile of Tertiary-Butyl Chloride Grignard Reagent in Diethyl Ether

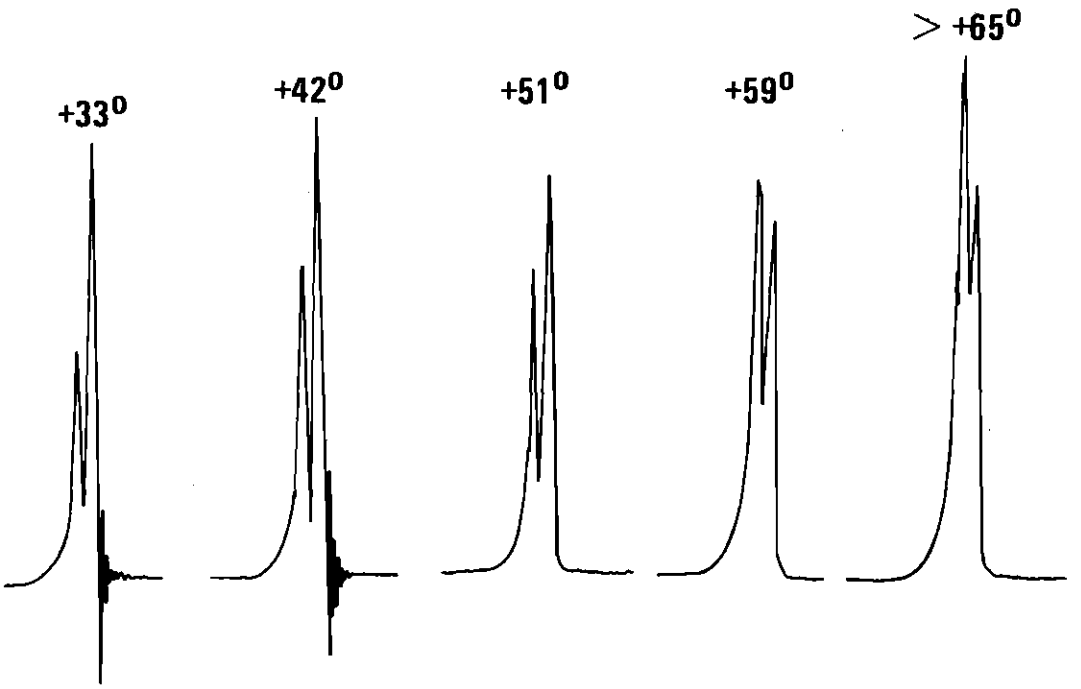


Figure 8. Proton Magnetic Resonance Profile of
Tertiary-Butyl Chloride Grignard Reagent in Tetrahydrofuran

diethyl ether a single signal is observed for the t-butyl group at 9.09τ. At -26° this signal is resolved into two signals (9.09 and 9.11τ) with the lower field signal being much more intense. By analogy with the methyl Grignard systems, these signals are assigned to solvates of t-butylmagnesium respectively. Two observations should be made. First, as in the case of the methyl Grignard reagents, the Schlenk equilibrium favors the RMgX solvate at room temperature. Second, alkyl exchange is much slower for the t-butyl system than the methyl system.

In tetrahydrofuran t-butyl chloride Grignard reagent exhibits two signals at 9.13 and 9.15τ at +33°. As shown in Figure 8, these signals do not coalesce at +65°, though as the temperature is raised the ratio of the two signals change. In analogy to all previous cases, these signals are assigned to solvates of t-butylmagnesium chloride (9.13τ) and di-t-butylmagnesium (9.10τ). The equilibrium constant for the Schlenk equilibrium and an estimate of the pre-exchange lifetime of the t-butyl groups between the non-equivalent sites was obtained at each temperature by calculating trial spectra using the DNMR computer program. This technique is of little use for determining activation parameters for alkyl exchange since the line broadening is so small. However, it is estimated that the pre-exchange lifetime of a t-butyl group is approximately 4 seconds at +42°. The natural logarithm of the calculated equilibrium constants was plotted against the inverse of the absolute temperature as shown in Figure 9 and tabulated in Table 4. The enthalpy for the forward reaction was calculated to be +9.0 kcal/mole while at +42° the entropy was 15 cal/deg·mole. The errors indicated for the low temperature points in Figure 9 correspond to the estimated

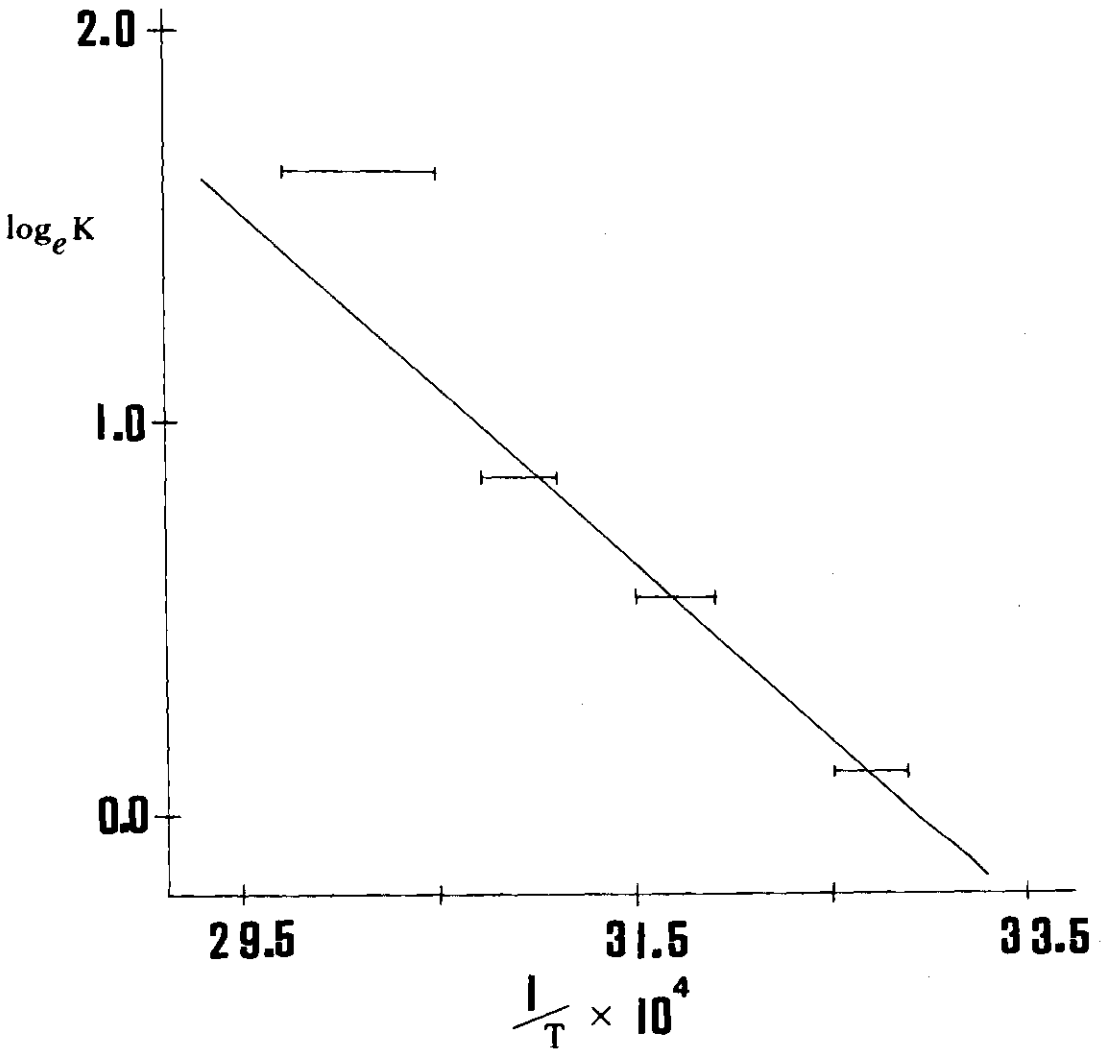


Figure 9. Plot of Ln K_{eq} Versus 1/T for Tertiary-Butyl Chloride Grignard Reagent in Tetrahydrofuran

Table 4. Thermodynamic Parameters for the Reaction

$$(t\text{-Bu})_2Mg + MgCl_2 \rightleftharpoons 2\ t\text{-BuMgCl}$$

Temperature °C	K	ln K	1/T
< + 65	7.54	2.02	< 0.00296
~ + 59	5.00	1.62	~ 0.00301
+ 51	2.36	0.859	0.00309
+ 42	1.74	0.554	0.00317
+ 33	1.12	0.109	0.00327

precision of ∿2° in the temperature measurements below +59°. The temperature control was unstable at +59° and a larger estimate of error has been applied. The equilibrium constant of 7.54 was obtained in a qualitative high temperature run and is intended to strengthen the qualitative arguments rather than for use in the thermodynamic experiments. In the equation, $R_2Mg + MgX_2 \rightleftharpoons 2\ RMgX$, no solvent is indicated but the endothermic nature of the reaction probably reflects loss of solvation energy from the magnesium halide solvate. The entropy effect is also consistent with a net loss of solvation.

It was of interest to study the effects of concentration on the position of the Schlenk equilibrium. Samples were prepared with a concentration range of 0.12 M to saturation. At concentrations below 3.1 M, no detectable change in the position of the Schlenk equilibrium occurred at room temperature. In the more concentrated solutions there may be a tendency to favor the RMgX component. The two signals were not resolved but the peak of the signal which was observed was more nearly the chemical shift (relative to TMS) of RMgX than R_2Mg. A slight downfield shift was noted for the solvent high field signal (relative to TMS), at these high concentrations, accompanied by loss of resolution resulting from viscosity or exchange. The low field THF signal was used as a lock and was not observed.

In the course of these studies, it was observed that air oxidation of samples of t-butylmagnesium chloride in THF resulted in signals in the region of 8.80τ as expected for the t-butoxyl group. See Figure 10. It was found that in solutions containing these alkoxide impurities, coalescence of the signals for RMgX and R_2Mg could be achieved at ∿+40°

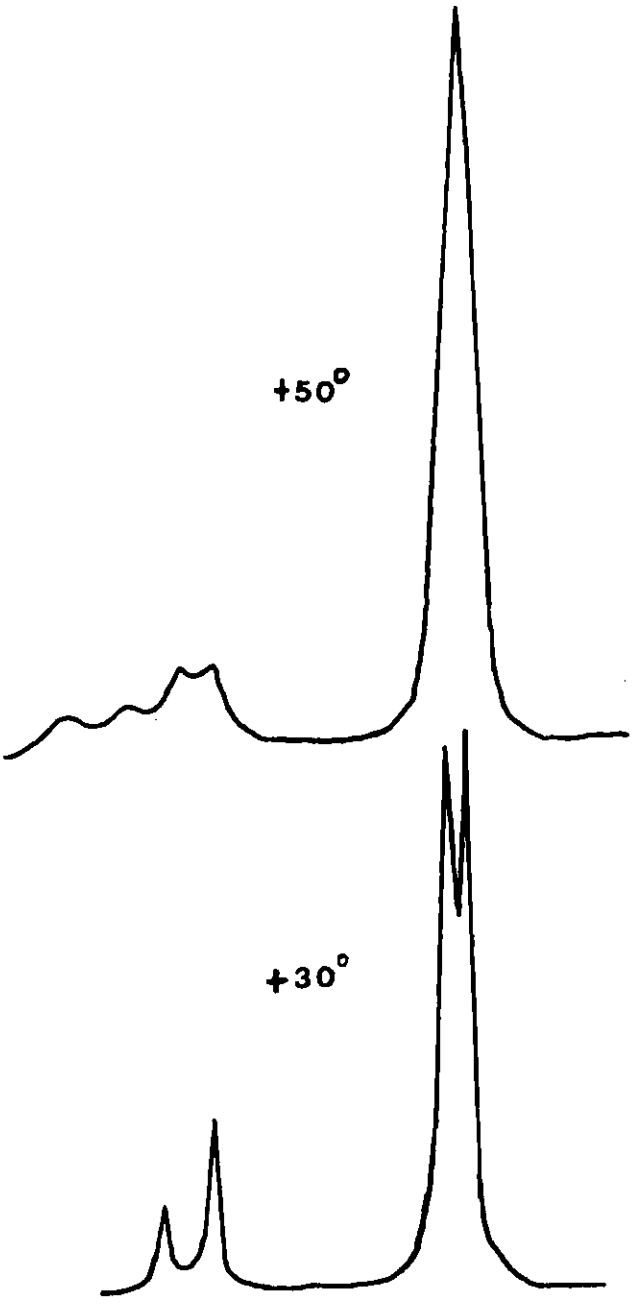


Figure 10. Proton Magnetic Resonance Spectra of Tertiary-Butyl Grignard Reagent in Tetrahydrofuran Containing Air Oxidation Products

whereas pure solutions were not observed to coalesce at +65°. Thus, the alkoxide impurities seemed to catalyze the exchange of alkyl groups between R_2Mg and RMgX.

CHAPTER IV

DISCUSSION

General

Proton magnetic resonance has been shown to be an effective tool for identifying the RMgX and R_2Mg components of the Schlenk equilibrium. However, experimental difficulties associated with these studies limit the use of computer simulation techniques in determining the position of the equilibrium or the rate of alkyl exchange. In the following paragraphs an attempt will be made to draw together the results of the preceding chapter and results found in recent publications into concise analyses of the factors governing the position and dynamics of the Schlenk equilibrium.

Concerning the Position of the Schlenk Equilibrium

While various "extended" forms of the Schlenk equilibrium have periodically been introduced to describe the solution composition of Grignard reagents with some justification, this broad view has tended to make the Grignard composition problem so complex as to be intractable. Thus, even at the risk of oversimplification, it is beneficial to try to enumerate some basic principles bearing on Grignard reagent composition in solution.

The most overlooked, yet perhaps the most important, factor in determining the position of the Schlenk equilibrium and subsequently the solution composition of the Grignard reagents is the role of solvent.

Clearly, it is shortsighted to attempt to describe the thermodynamic behavior of the Schlenk equilibrium on the basis of equilibrium 1 alone

$$R_2Mg + MgX_2 \rightleftharpoons 2\ RMgX \qquad (1)$$

when, in fact, each component has very specific interactions with the solvent. It is proposed that a more realistic and useful description of the Schlenk equilibrium should consider the specific interaction of each component in equilibrium 1 with the solvent.

$$N\ R_2Mg + \infty\ S \rightleftharpoons \sum_i n_i R_2Mg \cdot iS + [\infty - \sum_i (n_i)i]S$$

$$N\ MgX_2 + \infty\ S \rightleftharpoons \sum_j n_j RMgX \cdot jS + [\infty - \sum_j (n_j)j]S$$

$$N\ RMgX + \infty\ S \rightleftharpoons \sum_k n_k MgX_2 \cdot kS + [\infty - \sum_k (n_k)k]S$$

The equations above, where $N = \sum_1 n_1$, consider the reaction of each of the components of equilibrium 1 with an infinite amount of solvent to yield a number (i, j, k) of different solvates. It would be very cumbersome to carry this rigorous approach very far. Fortunately, it is possible to consider only one or two principal solvates for most real situations. The types of solvates and the number of types of solvates to which this simplification should be limited must be decided from actual experimental observation of the interaction of a specific component (R_2Mg, MgX_2, RMgX) with a specific solvent (S) under a given set of conditions of concentration and temperature. For example, some systems may be adequately described by only one type of solvate (e.g., mono- or di-

solvates) while another system may require consideration of two or more types of solvates in equilibrium (e.g., mono- and di- solvates or di- and tetra- solvates).

A simple representation of the basic solvation equilibrium is:

$$M \cdot S \rightleftharpoons M + S \qquad (2)$$

The forward reaction should be endothermic ($\Delta H > 0$) since a coordinate bond breaks and the entropy should be positive ($\Delta S > 0$) since the partition function for two particles (molecules) translating independently should be greater than that for the vibration of the coordinate bond (e.g., a vibrational degree of freedom is converted to a translational degree of freedom). The magnitude of the enthalpy change (ΔH) is generally closely approximated by the coordinate bond energy and the entropy change (ΔS) is frequently compared to the entropy of fusion of the solvent. That is, the coordinated solvent is considered to be "frozen" while the free solvent is regarded as "melted" (30). From this analysis, it is clear that high temperatures favor the forward reaction while low temperatures favor the reverse reaction.

Now that the principles involved have been discussed, it is helpful to introduce some experimental evidence for the state of solvation of several compounds of interest by various solvents. In general, the susceptibility of the components of equilibrium 1 to solvation increases in the order $R_2Mg < RMgX < MgX_2$. This order reflects the electrophilicity of the magnesium atom induced by the degree of ionic character in the R-Mg and Mg-X bonds. The polarity of the solvent also plays a large role in the preferred state of solvation. Finally, the steric strain of

the combined interactions of solute with coordinating solvent and between coordinate solvent molecules is the chief factor setting an upper limit on the degree of solvation (32).

Unhindered diorganomagnesium components, including the relatively bulky di-t-butylmagnesium (31), appear to prefer to form disolvates with tetrahydrofuran. Also, most evidence indicates that bis(diethyl etherates) of diorganomagnesium compounds form, although it would not be surprising to find that there is an appreciable concentration of mono-(diethyl etherate) in solutions of the more hindered compounds (33). Dicyclopentadienylmagnesium might be regarded as an exceptionally hindered diorganomagnesium compound. Diethyl ether probably does not form specific solvates with dicyclopentadienylmagnesium and the same can probably be said for tetrahydrofuran though the potential for ionization of this compound in very polar solvents could lead to strong interactions with the solvent.

Typical organomagnesium halides have been shown to form disolvates with diethyl ether (34,35,36). The same is probably true for tetrahydrofuran (37) though in the case of methyl bromide Grignard a tris(tetrahydrofuranate) has been crystallized (38). The formation of bis(diethyl etherates) and tris(tetrahydrofuranates) can probably be considered to be the upper limits of solvation of RMgX compounds in solution.

Magnesium halides appear to follow this order for solvation, $MgCl_2 < MgBr_2 < MgI_2$. With tetrahydrofuran tetrasolvates have been isolated (39) though with diethyl ether disolvates (40) appear to be the rule. Very ionic magnesium salts such as the perchlorates or

tetrafluoroborates which are not encountered in Grignard reagent systems probably form hexasolvates, $[MgS_6]X_2$.

Consider the solvation models described below. It is proposed that such models may be used to approximate actual Grignard reagent systems. The enthalpy (ΔH) and entropy (ΔS) changes associated with each model reflect the changes in the state of solvation of the system as the reaction proceeds from left to right. In an actual situation an equilibrium between two or more solvates of one or more of the components of the equilibrium might have to be considered such that at high temperature one model would be more accurate while at low temperature another model would be more accurate.

$$R_2Mg + MgX_2 \cdot 2S + 2\,S \rightleftharpoons 2\,RMgX \cdot 2S \qquad (1a)$$

ΔH very large, negative
ΔS very large, negative

$$R_2Mg \cdot S + MgX_2 \cdot 2S + S \rightleftharpoons 2\,RMgX \cdot 2S \qquad (1b)$$

ΔH large, negative
ΔS large, negative

$$R_2Mg \cdot 2S + MgX_2 \cdot 2S \rightleftharpoons 2\,RMgX \cdot 2S \qquad (1c)$$

ΔH small
ΔS small

$$R_2Mg + MgX_2 \cdot 4S \rightleftharpoons 2\,RMgX \cdot 2S \qquad (1d)$$

ΔH small
ΔS small

$$R_2Mg \cdot 2S + MgX_2 \cdot 4S \rightleftharpoons 2\,RMgX \cdot 3S \qquad (1e)$$

ΔH small
ΔS small

$$R_2Mg \cdot 2S + MgX_2 \cdot 4S \rightleftharpoons 2\ RMgX \cdot 2S + 2\ S \qquad (1f)$$

ΔH very large, positive
ΔS very large, positive

ΔH and ΔS in these models, 1a through 1f, refer only to the effects expected for changes in net solvation.

The principle used in proposing this scheme is that in any solvent the degree of solvation of the components will be in the order $R_2Mg < RMgX < MgX_2$. Thus, a system like

$$R_2Mg \cdot 2S + MgX_2 \rightleftharpoons 2\ RMgX \cdot S$$

is not reasonable and such an inclusion in the above listing would add unnecessary confusion. In addition, the cases noted above with completely unsolvated R_2Mg components are probably only applicable to dicyclopentadienylmagnesium. Ordinary unhindered Grignard reagents in diethyl ether are most likely to conform to models 1c or 1b. In tetrahydrofuran, models 1e and 1f are most viable. Finally, it should be noted that there has been no inclusion of bidentate solvents in the systems noted above. The effect of bidentate solvents can be predicted by realizing that the entropy (negative) of complexation with a Lewis acid will be unusually small per coordinate bond formed (the chelate effect).

The thermodynamic data available for the Schlenk equilibrium have come from several sources and are compiled in Table 5. In general, the trends predicted from a consideration of the effect of solvation are observed in the measurements made at or above room temperature. The thermodynamic parameters determined at low temperature are relatively

Table 5. Thermodynamic Data for the Schlenk Equilibrium

$$R_2Mg + MgX_2 \rightleftharpoons 2\ RMgX$$

Reference	R	X	S	ΔH (kcal/mole)	ΔS (cal/deg·mole)	
30	Et	Br	THF	6.1	23.7	(+25°)
30	Et	Cl	THF	3.8	16.1	(+25°)
9	t-Bu	Cl	THF	9.0	15	(+42°)
11	Ph	Br	THF	13.3	56	(-50°)
30	Ph	Br	THF	2.8	12.1	(+25°)
30	Ph	Cl	THF	2.7	10.1	(+25°)
11	2,6-DiMePh	Br	THF	8.0	56	(-40°)
11	2-CF_3Ph	Br	THF	0.0	22	(-30°)
11	2-CF_3Ph	Br	2-MeTHF	13.5	75	(-20°)
11	Ph	Br	2-MeTHF	-10.6	-20	(-75°)
12	Cp	Br	THF	7.3	45	(-75°)
12	Cp	Cl	THF	5.1	34	(-75°)
29	Et	Br	Et_2O	-3.7	-0.3	(+25°)
29	Et	I	Et_2O	-4.9	-1.2	(+25°)
29	Ph	Br	Et_2O	-2.0	1.2	(+25°)
29	Ph	I	Et_2O	-3.0	-0.1	(+25°)

Me = CH_3- Ph = C_6H_5-

Et = CH_3CH_2- Cp = C_5H_5-

t-Bu = $(CH_3)_3C$- THF = Tetrahydrofuran

erratic. In cases where the solvation models would predict small or perhaps even negative enthalpies and entropies, the values calculated from measurements in the -30° to -75° range are often large and positive. Reservations concerning the low temperature measurement of equilibrium constants have already been stated. If there were an equilibrium of the type

$$MgX_2 \cdot nS \text{ (solid)} \rightleftharpoons MgX_2 \cdot nS \text{ (solution)}$$

involved at low temperature, the effect would be reflected in the calculated thermodynamic parameters essentially as the enthalpy and entropy of fusion of the $MgX_2 \cdot nS$ (solid). A fairly obvious example of this behavior can be found in the case of the methyl bromide Grignard reagent in diethyl ether discussed in Chapter III. The thermochemical measurements at room temperature for the very similar ethyl bromide Grignard in diethyl ether show small negative enthalpies and entropies of reaction (ΔH = -3.7 kcal/mole, ΔS = -0.3 cal/deg·mole at 25°) (29). Lowering the temperature should drive the reaction in favor of RMgX as long as no other equilibria intervene and the absence of any appreciable shift in the PMR signal between +30° and -70° (Figure 5) bears out this expectation. However, below -70° the equilibria can no longer be approximated by model 1b or 1c since the crystallization studies suggest formation of a halide rich solid phase. The actual situation is more correctly described by the equilibrium

$$R_2Mg \cdot 2S \text{ (solution)} + MgX_2 \cdot 2S \text{ (solid)} \rightleftharpoons 2\ RMgX \cdot 2S \text{ (solution)}$$

where ΔH and ΔS are large and positive due to the phase change. There

is currently insufficient data to judge the credibility of thermodynamic parameters calculated for other systems on data obtained at low temperature by PMR spectroscopy. However, the only example where the same system (C_6H_5MgBr/THF) has been studied at +25° by calorimetric techniques and at -50° by proton magnetic resonance show significant discrepancies (Table 5).

Thus far, the arguments concerning the thermodynamics of equilibrium 1 have operated on the assumption that the bond energies of the R-Mg, Mg-X and Mg-S bonds are the same in all components in the Schlenk equilibrium. In most cases this assumption is not rigorously correct. For example, it has been shown that the redistribution of dimethylmercury with mercury(II) halides is favored by a sizable enthalpy effect (ΔH = -3 to -7 kcal/mole) in spite of the absence of appreciable solvent effects. This enthalpy change can be attributed to a more favorable heat of formation of the compound containing a combination of electropositive and electronegative groups (RHgX) than only electropositive groups (R_2Hg) or only electronegative groups (HgX_2) (41). It is likely that this bond energy effect is the primary effect on the enthalpy of reaction for Schlenk equilibria where there is little net gain or loss of solvation (1c, 1d, 1e). Similarly, in the case of solvation model 1f, the unfavorable (large, positive) enthalpy effects due to loss of solvation will be partially offset by favorable bond energy effects.

$$\Delta H_{\text{reaction}} = \Delta H_{\text{solvation}} + \Delta H_{\text{bond energy}}$$

It is probably worth noting that the favorable enthalpy of forming coordinate bonds is partially offset by unfavorable steric

interactions between the coordinate solvent molecules. Thus, ΔH for forming a tetrasolvate is probably considerably less than twice the enthalpy for forming a disolvate of the MgX_2 component. While the total enthalpy of solvation of a particular compound reflects both the number and average energy of the coordinate bonds formed, the average energy of coordinate bond formation probably follows the general trend,

$$MgX_2 \cdot 2S > MgX_2 \cdot 4S > RMgX \cdot 2S > R_2Mg \cdot S > RMgX \cdot 2S$$

To complete the discussion of the thermodynamics of the Schlenk equilibrium, it is important to consider the effect of association equilibria as invoked in the "extended" versions of the Schlenk equilibria. In general, association competes with solvation as a mechanism by which the coordination sphere of R_2Mg, RMgX and MgX_2 compounds are satisfied.

$$YMgZ \cdot S + S \rightleftharpoons YMgZ \cdot 2S$$

$$2\ YMgZ \cdot S \rightleftharpoons (YMgZ \cdot S)_2$$

The effect of association of a component in the Schlenk equilibrium is to reduce the concentration (activity) of that component in the equilibrium.

One system which has received considerable study is the ethyl chloride Grignard reagent in tetrahydrofuran (27,30,32). Smith and Becker (30) obtained the thermochemical results shown below:

$$EtMgCl + MgCl_2 \rightleftharpoons EtMg_2Cl_3$$

At 25°,
$\Delta H = 1.0$ kcal/mole
$\Delta S = 6.4$ cal/deg·mole

The driving force for this reaction also seems to be related to the large, positive entropy of freeing solvent from the $MgCl_2$ component, even at the expense of association. In the solid phase, even higher aggregation to a tetrameric unit occurs with presumably more loss of solvent (32).

Secondary reactions of the organomagnesium halide with magnesium halide do not appear to be universal. Not only is there little evidence for this type reaction for halides other than chloride, but also Smith and Becker (30) observed that phenyl chloride Grignard reagent in tetrahydrofuran did not reveal this behavior. Therefore, the straightforward technique used to calculate equilibrium constants for tertiary-butyl chloride Grignard in tetrahydrofuran is justified.

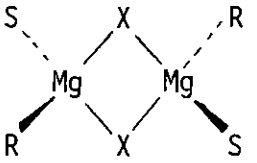
There is nothing particularly novel about the above arguments. The thermodynamic arguments are straight out of elementary physical chemistry texts. Other workers, particularly Smith and Becker (28,29, 30), are primarily responsible for this approach to understanding, predicting and ultimately controlling the composition of the Grignard reagents in solution. The justification for the sometimes tedious elaboration on the basic concepts which have been in the literature for nearly a decade is that they have been largely ignored. Finally, the principles emphasized here are just as valid for organometallic compounds of other main group metals (e.g., beryllium, aluminum, zinc, cadmium and

mercury) as for the Grignard reagents.

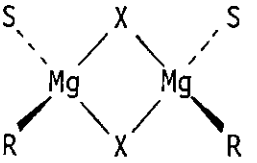
Concerning the Dynamics of the Schlenk Equilibrium

There are three primary dynamic processes occurring within the Grignard reagent solution. First, there is exchange of solvent molecules coordinated to the organometallic compounds with bulk solvent. Second, there is exchange of like groups (R with R or X with X) between magnesium centers. Third, there is exchange of unlike groups between magnesium centers (R with X).

The question of how rapidly coordinated solvent exchanges with bulk solvent relates to a number of problems. For example, it is reasonable that cis- and trans- forms of dimers of the type

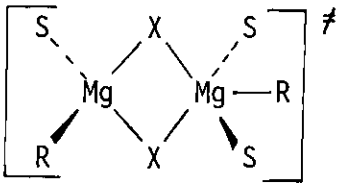


trans- dimer

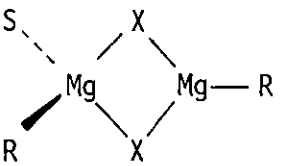


cis- dimer

exist in similar concentrations because the free energy difference between them should be small. However, since a simple mechanism for interconversion of the cis- and trans- isomers can be described without breaking any bonds except those to solvent by an S_n1 or S_n2 type solvent



S_n2
(associative exchange)



S_n1
(dissociative exchange)

exchange, is it reasonable to expect to see these isomers in the PMR spectrum? Similarly, if in a given system several different solvates occur in similar abundance, could these be readily detected by PMR spectroscopy? The answer to these questions is illusive. From the meager knowledge of the rate of exchange of polar solvents such as water between the coordination sphere of non-transition elements and the bulk solvent, it can be argued that as the charge density on the metal increases the rate of exchange decreases. For example, Mg^{2+}, Ba^{2+}, Sn^{2+}, Hg^{2+}, all exchange water at a rate much greater than 10^4 sec^{-1}, but Be^{2+} exchanges solvent at a rate of approximately 10^3 sec^{-1} and Al^{3+} exchanges water at about 10^1 sec^{-1} (42). Since the strength of the coordinate bond of the less polar ethers to the less ionic organometallic compounds are weaker, more rapid rates of solvent exchange would be expected for these systems. Unfortunately, there is no directly applicable evidence for the rate of solvent exchange in organomagnesium compounds, but the time scale of PMR resolution is determined by

$$k \equiv (w_A - w_B)$$

where w_A and w_B are the relative chemical shifts in cycles per second (Hz). Thus, if the two signals are 100 cps apart and the rate of exchange (k) is much greater than 10^2 sec^{-1}, there would be little detectable broadening of the PMR average exchange signal. Therefore, it is probably unwise to indiscriminately assign signals in PMR spectra to different solvates of the same compound even at low temperatures.

On the other hand, Kovar and Morgan have demonstrated convincingly that they resolved separate signals for mono- and di- solvates of

dimethylberyllium in dimethyl sulfide (25). Though they did not elaborate on the observation, their data suggest that the pre-exchange lifetime of $S(CH_3)_2$ coordinated to $(CH_3)_2Be{\cdot}2S(CH_3)_2$ must be at least 10^{-1} sec at -50° since the rate of methyl exchange between the methyl sites of the mono- and di- solvates is on the order of 10^{1} sec^{-1} and exchange of coordinated solvent with bulk solvent is a mechanism which results in methyl exchange between the two sites.

$$(CH_3)_2Be{\cdot}2S(CH_3)_2 \rightleftharpoons (CH_3)_2Be{\cdot}S(CH_3)_2 + S(CH_3)_2$$

Thus, finding evidence for solvent exchange by PMR may be a matter of looking more closely for it.

Alkyl exchange in organometallic systems has occasionally been referred to as electrophilic aliphatic substitution. The groups of Hughes and Ingold (43,44) are primarily responsible for developing this area in terms of mechanism and language with their study of organomercurials in the 1950's. In analogy to the nucleophilic substitution mechanisms, S_E1, S_E2 and S_Ei mechanisms of exchange have been considered.

S_E2 $\quad XHg^+ + RHgY \xrightarrow{slow} XHgR + YHg^+$

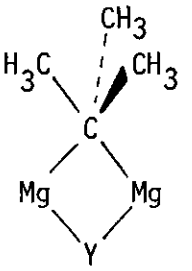
S_Ei $\quad XHgZ + RHgY \xrightarrow{slow} RHgX + YHgZ$

S_E1 $\quad RHgY \xrightarrow{slow} R^- + YHg^+$

$\quad XHg^+ + R^- \xrightarrow{fast} RHgX$

The S_E1 mechanism is a reasonable suggestion only when a particularly stable organo-anion is produced. This requirement probably limits its occurrence to enolate anions and perhaps the cyclopentadienyl, indenyl

or fluorenyl anions in polar solvents. For the common alkyl and aryl Grignard reagents the S_E2 or S_Ei mechanisms are the only likely candidates to account for exchange. Three characteristics of the S_Ei mechanism are, first, that a mixed-bridge intermediate or transition state be formed, second, that alkyl exchange should occur with retention of configuration at carbon and third, the exchange should follow second order kinetics. All of these characteristics are commonly observed in organomagnesium exchange reactions. In the case of t-butyl- versus methyl-exchange mentioned in Chapter III, it is arguable that the great decrease in the rate of exchange in going from methyl- to t-butyl-Grignard systems is due to the unfavorable steric requirement of putting the t-butyl group in a bridging position.



The arguments which are normally made against S_N2 substitution at tertiary carbon can be applied to S_E2 substitution. At the same time, it was observed that alkoxide impurities catalyze exchange probably by stabilizing the mixed bridge species (45).

While no work was done here relating to inversion or retention of configuration of the exchanging alkyl group, studies which have been carried out (7,8,15) indicate that there is inversion but its rate is much slower than the rate of exchange. Thus, exchange occurs primarily

with retention of configuration as required by the $S_E i$ mechanism. However, the $S_E 2$ mechanism may also be operative to an extent sufficient to account for the rate of inversion (15).

Finally, as observed when comparing the rate of exchange of methyl- or t-butyl- Grignards in diethyl ether and tetrahydrofuran, it has been shown in a number of studies (8,9,11,12,46) that more polar and particularly bidentate solvents slow the rate of exchange significantly. House and co-workers (8) were the first to introduce the concept of a preliminary desolvation equilibria to produce a coordinately unsaturated organomagnesium species which is the reactive species in exchange. Derivation of the appropriate kinetic equation is found in Appendix 3. Their suggestion seems to be very well established and once again underscores the importance of solvation in the composition of organometallic reagents.

CHAPTER V

CONCLUSIONS

It can be concluded from the preceding chapters that solvation plays the dominant role in determining the composition of the Grignard reagents in solution because it is not only the primary factor determining the position of the Schlenk equilibrium, it is also the factor which most affects association equilibria and even the dynamics of exchange reactions. It should be further concluded that these principles apply to virtually all organometallic reagents where ligand field stabilization effects are not important. Of course, some modifications of the quantitative arguments are required. For example, the tendency to form etherates varies more or less in the order $(CH_3)_2Mg > (CH_3)_2Be > (CH_3)_2Zn > (CH_3)_2Cd > (CH_3)_2Hg$, but even in organomercury halide systems the Schlenk type equilibrium can be driven to the left by the addition

$$R_2Hg + HgX_2 \rightleftharpoons 2\ RHgX$$

of a solvent such as pyridine which coordinates strongly with the HgX_2 component. Thus, the principles of solvation apply. It is found that coordination of the RHgX compounds with polar solvents or halide ions in rapid pre-equilibria to give RHgX·S species catalyzes alkyl exchange (44). The principle is similar to the rapid pre-exchange equilibria found in alkyl exchange reactions of magnesium reagents (8). Thus, the most important conclusion is that there are underlying principles in

organometallic chemistry which can be used to systematize a large body of data on many compounds of many metals.

APPENDIX 1

INPUT DATA FOR THE DNMR PROGRAM

There are eight important data cards required for execution of the DNMR program for simulation of an exchange-broadened nuclear magnetic resonance spectrum. An example of the input data used in this problem is listed below.

Card Number — Columns

I

```
1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20
1  0  1  1  2  0
```

- `1 0 1` — non-zero identification number
- `1` — one type nucleus
- `2` — two magnetic sites
- `0` — denotes independent exchange

II

```
1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20
                  E  Q  U  I  L  I  B  R  I  U  M     1
```

III

```
1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20
1  0  .  0
```

`1 0 . 0` — Chemical shift (in Hz) of RMgX (site 1) relative to arbitrary reference

IV

```
1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20
1  1  .  6
```

Chemical shift (in Hz) of R_2Mg (site 2) relative to arbitrary reference

V

```
1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20
0  1  0  1                          0  .  0
```

left plot frequency XMIN (in Hz)

plotter output requested

no card output requested

number of sets of rate constants

```
21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40
2  0  .  0                          4  .  0
```

horizontal plot scale (in mm/Hz)

right plot frequency XMAX (in Hz)

```
41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60
1  3  2  .  0
```

height of highest peak in spectrum (in mm), limited to 240 mm

Note: This card sets the parameters used by the CALCOMP plotter to ensure that the generated spectrum is on the same scale as the experimental spectrum. The generated spectrum will begin at an arbitrary chemical shift of 0.0 Hz and continue to 20.0 Hz. From cards III and IV it is evident that there will be peaks at 10.0 Hz and 11.6 Hz.

VI 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

0 . 3 4 8 0 . 6 5 2

populations of sites 1 and 2 respectively
These populations were varied until the computed spectrum matched the experimental spectrum.

VII 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

0 . 4 2 5

effective transverse relaxation time (T_2)

$$T_2 = \frac{1}{\pi W_{1/2}}, \qquad \pi = 3.14159 \quad \text{and}$$

$W_{1/2}$ is the full-width at half-height of a single peak <u>not</u> broadened by exchange. The tetramethylsaline signal was used for calculating T_2 in these spectra.

VIII 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

0 . 1 5

rate of exchange $K_1 = \frac{1}{\tau_1}$ (sec^{-1}) where τ_1 is the pre-exchange lifetime of a tert-butyl group in site 1 (RMgX).

Notice that $\frac{K_1}{K_2} = \frac{\tau_2}{\tau_1} = \frac{P_2}{P_1}$ where P_1 and P_2 are the populations of sites 1 and 2 respectively.

APPENDIX 2

APPLICATION OF THE WEIGHTED AVERAGE LAW FOR EXCHANGING SYSTEMS TO THE SCHLENK EQUILIBRIUM

Definitions

δ_{Avg} = exchange averaged chemical shift

δ_i = chemical shift of component i in the absence of exchange

N_i = mole fraction of component i

The Weighted Average Law

$$\delta_{Avg} = \sum_i N_i \delta_i \tag{1}$$

$$1 = \sum_i N_i \tag{2}$$

The Schlenk Equilibrium

$$R_2Mg + MgX_2 \rightleftharpoons 2\ RMgX$$

$$K = \frac{[RMgX]^2}{[R_2Mg][MgX_2]} = \frac{[RMgX]^2}{[R_2Mg]^2} \tag{3}$$

Since the PMR signals represent methyl groups rather than magnesium atoms, equation 3 converts to equation 4.

$$K = \left[\frac{N_{RX}}{1/2\ N_{RR}}\right]^2 = 4\left[\frac{N_{RX}}{N_{RR}}\right]^2 \tag{4}$$

Derivation

From equations 1 and 2

$$N_{RR} = \frac{\delta_{Avg} - \delta_{RX}}{\delta_{RR} - \delta_{RX}} \tag{5}$$

Letting $N_{RR} = x$ for computational purposes,

$$K = 4\left[\frac{1-x}{x}\right]^2 \pm 8\left[\frac{1-x}{x^3}\right] dx \tag{6}$$

where the error term is simply

$$dK = \sqrt{(f'(x)dx)^2}$$

The uncertainty in x, dx, is based on the expected error of 1.0 cps in measuring the chemical shifts. It is obvious that the relative error in K, dK/K, is minimized when K = 4. When K tends to be larger or smaller, the uncertainty in this technique can become so large that it is only practical to state to which side the equilibrium lies. In the case of the methyl Grignard reagents in tetrahydrofuran where $\delta_{RR} = 11.76$, $\delta_{RX} = 11.64$ and $\delta_{Avg} = 11.70$ (X = Br), $\delta_{Avg} = 11.72$ (X = Cl), an error of 1.0 cps in δ_{Avg} would lead to an error in x of about 0.08 since,

$$\frac{0.01}{11.76 - 11.64} = \frac{0.01}{0.12} = 0.08$$

The calculated equilibrium constants are 4 ± 2.6 and 1 ± 0.72 for X = Br and X = Cl respectively based on the assumptions of chemical shifts noted above.

APPENDIX 3

EFFECT OF THE RAPID DESOLVATION EQUILIBRIUM UPON THE RATE OF INTERMOLECULAR ALKYL EXCHANGE

Mechanism of Alkyl Exchange

fast $$RMgX\cdot 2S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RMgX\cdot S + S$$

fast $$R_2Mg\cdot 2S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2Mg\cdot S + S$$

slow $$R^*MgX\cdot S + R_2Mg\cdot S \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RMgX\cdot S + RMgR^*\cdot S$$

Derivation

$$k_{exchange} = k_3[RMgX\cdot S][R_2Mg\cdot S]$$

$$[RMgX\cdot S] = \frac{k_1}{k_{-1}}\frac{[RMgX\cdot 2S]}{[S]} = \frac{K_1}{[S]}[RMgX\cdot 2S]$$

$$[R_2Mg\cdot S] = \frac{k_2}{k_{-2}}\frac{[R_2Mg\cdot 2S]}{[S]} = \frac{K_2}{[S]}[R_2Mg\cdot 2S]$$

$$k_{exchange} = k_3\,\frac{K_1}{[S]}\,\frac{K_2}{[S]}\,[RMgX\cdot 2S][R_2Mg\cdot 2S]$$

Obviously, as the solvent dissociation equilibria move more in favor of the reactive tricoordinate magnesium species the rate of exchange will increase. Also note that the rate of exchange should increase with concentration not only because the product $[RMgX \cdot 2S][R_2Mg \cdot 2S]$ increases but also because $[S]^2$ decreases.

LITERATURE CITED*

(1) E. C. Ashby, Quart. Rev., 21, 259 (1967).

(2) W. Schlenk and W. Schlenk, Jr., Ber., 62, B, 920 (1929).

(3) W. Schlenk, Ber., 64, B, 734 (1931).

(4) R. M. Salinger and H. S. Mosher, J. Amer. Chem. Soc., 86, 1782 (1964).

(5) D. F. Evans and J. P. Maher, J. Chem. Soc., 5125 (1962).

(6) D. F. Evans and M. S. Khan, Chem. Comm., 67 (1966).

(7) George M. Whitesides, Fred Kaplan and John D. Roberts, J. Amer. Chem. Soc., 85, 2167 (1963).

(8) Herbert O. House, Roger A. Latham and George M. Whitesides, J. Org. Chem., 32, 2481 (1967).

(9) G. E. Parris and E. C. Ashby, J. Amer. Chem. Soc., 93, 1206 (1971).

(10) E. C. Ashby, G. Parris and F. Walker, Chem. Comm., 1464 (1969).

(11) D. F. Evans and G. V. Fazakerley, J. Chem. Soc. (A), 184 (1971).

(12) W. T. Ford and J. B. Grutzner, J. Org. Chem., 37, 2561 (1972).

(13) D. A. Hutchison, R. R. Beck, R. A. Benkeser and J. B. Grutzner, J. Amer. Chem. Soc., 95, 7075 (1973).

(14) H. E. Zieger and J. D. Roberts, J. Org. Chem., 34, 1976 (1969).

(15) G. Fraenkel, C. E. Cottrell and D. T. Dix, J. Amer. Chem. Soc., 93, 1704 (1971).

(16) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill Co., New York, N. Y., 1969.

(17) E. C. Ashby and R. D. Schwartz, J. Chem. Educ., 51, 65 (1974).

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*Journal title abbreviations used are listed in "List of Periodicals", Chemical Abstracts, (1961).

(18) C. N. Reilley, R. W. Schmid and F. S. Sadek, J. Chem. Educ., 36, 619 (1959).

(19) D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry", Holt, Rinehart and Winston, New York, N. Y., 1963, pp. 254-258.

(20) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis, Vol. 1", John Wiley and Sons, Inc., New York, N. Y., 1967, p. 120.

(21) G. Binsch, J. Amer. Chem. Soc., 91 (1969).

(22) E. Weiss, J. Organometal. Chem., 2, 314 (1964).

(23) G. E. Coates and K. Wade, "Organometallic Compounds, Vol. I, The Main Group Elements", Third Ed., Methuen & Company, London, 1967, Chapter 2, p. 99.

(24) Frank W. Walker and E. C. Ashby, J. Amer. Chem. Soc., 91, 3845 (1969).

(25) R. A. Kovar and G. L. Morgan, J. Amer. Chem. Soc., 91, 7269 (1969).

(26) N. Muller and D. E. Prichard, J. Amer. Chem. Soc., 82, 248 (1960).

(27) E. C. Ashby and W. E. Becker, J. Amer. Chem. Soc., 85, 118 (1963).

(28) M. B. Smith and W. E. Becker, Tetrahedron Letters, 3843 (1965).

(29) M. B. Smith and W. E. Becker, Tetrahedron, 22, 3027 (1966).

(30) M. B. Smith and W. E. Becker, Tetrahedron, 23, 4215 (1967).

(31) G. E. Coates and J. A. Heslop, J. Chem. Soc. (A), 514 (1968).

(32) J. Toney and G. D. Stucky, J. Organometal. Chem., 28, 5 (1971).

(33) G. Stucky and R. E. Rundle, J. Amer. Chem. Soc., 86, 4825 (1964).

(34) L. J. Guggenberger and R. E. Rundle, J. Amer. Chem. Soc., 86, 5344 (1964).

(35) G. Stucky and R. E. Rundle, J. Amer. Chem. Soc., 85, 1002 (1963).

(36) G. Stucky and R. E. Rundle, J. Amer. Chem. Soc., 86, 4825 (1964).

(37) F. Schroder and H. Spandau, Naturwissen-Schaften, 53, 360 (1966).

(38) M. Vallino, J. Organometal. Chem., 20, 1 (1969).

(39) M. C. Perucand and M. T. LeBihan, Acta. Cryst. Sect. B, 24, 1502 (1968).

(40) H. Schibilla and M. T. LeBihan, Acta. Cryst., 23, 232 (1967).

(41) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Inc., Englewood Cliffs, N. J., 1970, pp. 37-39.

(42) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, pp. 151-156.

(43) E. D. Hughes and H. C. Volger, J. Chem. Soc., 2359 (1961).

(44) C. K. Ingold, Helv. Chem. Acta., 47, 1191 (1964).

(45) E. C. Ashby, J. T. Laemmle and G. E. Parris, J. Organometal. Chem., 19, P24 (1969).

(46) J. A. Magnuson and J. D. Roberts, J. Org. Chem., 37, 133 (1972).

PART II

THE STRUCTURE AND SOLUTION COMPOSITION OF CYCLOPENTADIENYLMETHYLMAGNESIUM IN BENZENE AND ETHER SOLVENTS

CHAPTER I

INTRODUCTION

Background

The cyclopentadienyl group is widely recognized to form a variety of bonds with metals (1-6). The factors governing the nature of the ring-metal interaction are the number, symmetry and energy of the metal orbitals. In the case of magnesium it seems clear that the interaction with a cyclopentadienyl ring should be essentially electrostatic (7,8) since the metal orbitals are of such high energy that any bond to carbon is highly polar (9,10). On the basis of electrostatic interaction, the approach of a magnesium ion is expected to be along the fivefold axis of the D_5h cyclopentadienyl anion. In the case of dicyclopentadienylmagnesium, it has been found experimentally that the cation polarizes the anion reducing its symmetry to C_5v and lowering the charge separation between the ions as though a covalent bond had been formed (11).

In addition to spectroscopic studies, an X-ray powder diffraction study revealed that dicyclopentadienylmagnesium is isostructural with ferrocene (12). More recently, examination of the tetraethylethylenediamine adduct of cyclopentadienylmagnesium bromide indicated that the cyclopentadienide anion in this compound is undistorted; the magnesium atom lies near the fivefold axis of the ring and the bond lengths suggest that the bonding should be described in terms of hexacoordination of the magnesium ion (13). House and co-workers (14) described a

bis(tetrahydrofuran) adduct of cyclopentadienylphenylmagnesium which seems to fall into this same general pattern. They also reported the preparation of cyclopentadienylmethylmagnesium as a non-solvated compound.

The reoccurring question concerning the interaction of the cyclopentadienyl group with magnesium involves the degree of covalent character of the metal-carbon bond. If the bond is basically covalent, then the magnesium will use only hybrids of s and p atomic orbitals for bonding and must be tetracoordinate, but if the bond is ionic, d as well as s and p atomic orbitals may be employed and hexacoordination results. The "logical" choice for a suggested structure for compounds such as cyclopentadienylmethylmagnesium, depends somewhat upon a person's predisposition regarding the nature of the cyclopentadienyl-magnesium bond.

Purpose

The experiments described below were undertaken because the initial literature description of cyclopentadienylmethylmagnesium (14) suggested that the compound might exist as an unsolvated monomer in solution and the solid phase (Figure 1). Such a molecule might provide a starting point for synthesis of a number of new organomagnesium compounds including C_5H_5MgH. All of these novel compounds would be potentially interesting reagents for stereoselective alkylation or reduction of organic substrates. Very early in the work it was found that the originally proposed structure (Figure 1) did not adequately describe the structure or composition of cyclopentadienylmethylmagnesium. Thus, the emphasis shifted from the experiments mentioned above to an attempt to

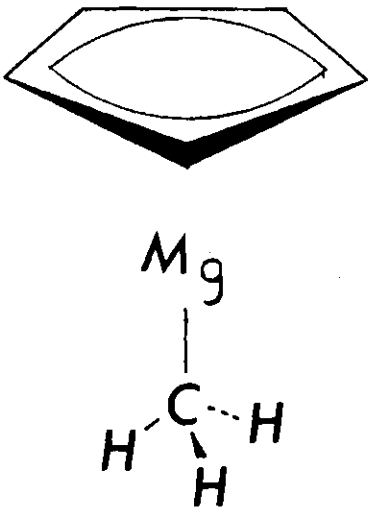
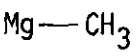
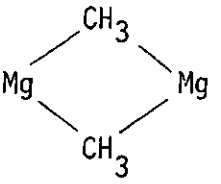


Figure 1. First Structure Proposed for Cyclopentadienylmethylmagnesium

determine the solid phase structure and solution composition of the compound. The three areas of most interest were the nature of the cyclopentadienyl-magnesium bond, the nature of the methyl-magnesium bond and solution phase equilibria involving the compound.

As these studies progressed, it became of interest to establish an infrared technique, applicable to both solution and solid phase studies, for distinguishing between the two most common forms of methyl-magnesium bonding.





CHAPTER II

EXPERIMENTAL

Synthesis and Analysis

General Procedures

All methyl- and cyclopentadienyl-magnesium compounds are air sensitive and all reactions were carried out with the aid of a dry box or syringes under nitrogen. Even the briefest exposure of magnesium cyclopentadienides to oxygen results in a red color. Hydrolysis in the absence of oxygen results in a yellow color.

All solvents were distilled from reactive hydrides prior to use (benzene and toluene from NaH, tetrahydrofuran from $NaAlH_4$ and diethyl ether from $LiAlH_4$). All spectroscopic samples were prepared in a nitrogen filled dry box equipped with a recirculating purification system.

Preparation of Dimethylmagnesium

Dimethylmagnesium was prepared by reacting neat dimethylmercury (Orgmet) with a 100% excess of sublimed magnesium metal (Dow) for 24 hr at room temperature. After evacuating to remove any unreacted dimethylmercury, the dimethylmagnesium was extracted with diethyl ether and the solution was filtered to remove the amalgam.

Distillation of Cyclopentadiene

Dicyclopentadiene is the Diels-Alder dimer of cyclopentadiene. To obtain cyclopentadiene (b.p. 41°), it was necessary to reflux fresh dicyclopentadiene (b.p. 170°) to crack the dimer and distill the more

volatile monomer (15). A reflux condenser filled with acetone (b.p. 56°) was found to be convenient for the separation. The monomer was condensed in a dry ice/acetone trap and used immediately after distillation. Prolonged reflux of the dimer results in formation of higher polymers which give poorer results.

Preparation of Cyclopentadienylmethylmagnesium Monoetherate

Freshly distilled cyclopentadiene (16 ml) was added to an ether solution of dimethylmagnesium (0.1 mole/200 ml) prepared from dimethylmercury. The reaction mixture was allowed to stand undisturbed at 20-25°. Methane evolved slowly and was vented through a mineral oil bubbler. After five days, a deposit of large, translucent crystals had formed. The crystals were filtered, washed with ether and dried briefly in a stream of nitrogen. A weighed sample was analyzed for the ratio of methane to magnesium and for percent magnesium by vacuum line techniques and EDTA titration. The result was methane:magnesium, 0.96:1.00. Calcd. for "$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$":Mg, 13.6%. Found: 13.7%. The yield of the monoetherate was 10.1 gr or 57% based on the dimethylmagnesium.

Dicyclopentadienylmagnesium was prepared similarly using longer reaction times (8 to 10 days) and a larger excess of cyclopentadiene. The soluble compound was isolated by removal of the solvent under vacuum. The product was purified by repeated sublimation in vacuo at ∿100°.

Vacuum Line Technique for Methane Analysis

Active methyl groups were analyzed by reacting samples with methanol on a high-vacuum line. The volume of evolved methane was determined by transferring the gas to a calibrated bulb via a Toepler pump.

Physical Studies

Desolvation of Cyclopentadienylmethylmagnesium Monoetherate

Large crystals (∿0.1 gr each) of "$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$" were desolvated on a vacuum line under a dynamic vacuum of ∿10^{-4} mm Hg at 20-25°. In three hours a 13% weight loss was observed, after one day the weight loss was 36% and after three days, 44% (theoretical weight loss is 41.5%). It was found that finely ground material could be totally desolvated in a few hours. Slow sublimation of the material, as in the thermal analysis experiment described below, resulted in sublimation of $(C_5H_5)_2Mg$ and a small amount of $C_5H_5MgCH_3$, leaving behind almost the theoretical amount of $(CH_3)_2Mg$.

Solubility

It was found that cyclopentadienylmethylmagnesium monoetherate is quite soluble in tetrahydrofuran and benzene (>0.5 m) but much less soluble in diethyl ether (∿0.12 m). When the ether was removed from finely ground "$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$" at 20-25° and the resulting "$C_5H_5MgCH_3$" covered with benzene and allowed to stand for six days at 20-25°, only traces of C_5H_5- and CH_3- were detected in the benzene by PMR. No ether was detected in the benzene. The solid rapidly dissolved when ether was added.

Alkylation of 4-t-Butylcyclohexanone

Solutions of cyclopentadienylmethylmagnesium monoetherate in ether and benzene (1.1 mmole/∿100 ml) were prepared. To these solutions were added solutions of 4-t-butylcyclohexanone in the same solvent (1.0 mmole/10 ml). The reaction mixtures immediately turned yellow (enolization of the ketone). The reaction mixtures were hydrolyzed and analyzed by

GLC (20 ft x 0.25 in copper column of 10% FFAP on Chromosorb W at 120° with 60 ml of He/min). The methylation product ratios were axial alcohol 70%, equatorial alcohol 30%, with an amount of starting ketone equal to the sum of the alcohols. The elution order and relative retention times were axial alcohol 2.52, starting ketone 3.14, equatorial alcohol 3.46. Hydrocarbon $C_{14}H_{30}$ is a good internal standard for this system with relative retention time 1.00. The methylation product ratio is not unusual. Similar results are obtained for most methylmagnesium compounds. No peaks assignable to addition of the C_5H_5 group to the ketone were observed. It is believed that most of the C_5H_5 groups acted to abstract protons causing enolization of the starting ketone.

Physical Methods of Analysis

Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer. Solid phase spectra were in fluorolube (4000-1350 cm^{-1}) or nujol (1375-200 cm^{-1}) mulls between cesium iodide plates. Solution phase spectra were obtained using 0.1 mm path length potassium bromide cells. A matching cell containing solvent was placed in the reference beam.

Proton magnetic resonance spectra were recorded on a 60 MHz Varian NMR spectrometer at probe temperature. Low temperature spectra were recorded on a 100 MHz Jelco NMR spectrometer.

Thermal analyses of cyclopentadienylmethylmagnesium etherate and dimethylmagnesium were performed on a Mettler Thermoanalyzer II modified for differential pressure recording at reduced pressure. The furnace was kept under a dynamic vacuum during the thermal analysis. The evolved gases were passed over a thermal conductivity detector, through a liquid nitrogen trap, past a second thermal conductivity detector and

then through a second liquid nitrogen trap to a mechanical pump. The outputs from the thermal conductivity detectors were compared. If a noncondensable gas such as H_2 or CH_4 was evolved, there was little pressure lag at the second detector caused by the intervening liquid nitrogen trap. On the other hand, the evolution of a condensable gas such as $(C_2H_5)_2O$ was observed at the first detector but not at the second. A large weight loss with little or no pressure effect was indicative of sublimation of the sample from the crucible to cooler parts of the apparatus. Details of the apparatus and procedure have been published (16).

The association of these compounds in benzene was studied by cryoscopy in an apparatus modified for handling air sensitive compounds. The association of "$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$" in diethyl ether was examined by the ebullioscopic technique developed in this laboratory (17). The results of all molecular association studies are tabulated in Appendix 2.

CHAPTER III

RESULTS AND DISCUSSION

Solid Phase Studies

The prominent features of the solid state structure of "$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$" can be deduced by comparison of its infrared spectrum with those of similar organometallic compounds: Dimethylmagnesium (18-20), dicyclopentadienylmagnesium (11), potassium cyclopentadienide (21,22), methyllithium (23) and dimethylberyllium (24,25). As shown in Table 1, the infrared-active cyclopentadienyl fundamentals of "$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$" are most consistent with D_5h ring symmetry. However, slight distortion towards either C_5v or C_s ring symmetry cannot be ruled out since the additional bands expected for distortion towards these lower symmetries would be weak and would fall into regions of the spectrum where methyl or ether bands occur (21,22,26). D_5h symmetry of the C_5H_5 anion is the limiting symmetry for weak ring-metal interactions regardless of whether the metal is on the fivefold axis (slight distortion towards C_5v symmetry) or on the perimeter of the ring (slight distortion towards C_s ring symmetry). The methyl fundamentals are similar to those of methyl compounds of other electropositive metals (23-25). In particular, the ν(C-H) bands occur at relatively low frequency and the $\delta_d(CH_3)$ band is not observed. On the other hand the $\delta_s(CH_3)$ band is not split into two bands as noted in the other spectra listed in Table 1. The skeletal vibration region (600-300 cm^{-1}) is dominated by several

Table 1. Comparison of Infrared Spectra of Methyl and Cyclopentadienyl Organometallic Compounds[a,b]

Vibrations	$(CH_3Li)_4$[c]	$[(CH_3)_2Be]_n$[d]	$[(CH_3)_2Mg]_n$	"$CpMgCH_3 \cdot Et_2O$"	"$CpMgCH_3$"
Methyl fundamentals					
ν(CH)	2840 2780	2912 2885	2850 2780	2865 2790	2860 2790
$\delta_d(CH_3)$	1480 1427				
$\delta_s(CH_3)$	1096 1061	1255 1243	1200 1186	1188	1185
$\rho_r(CH_3)$		835[e]	712	860	860

Vibrations	CpK[f] (D_5h ring)	CpLi[f] (C_5v ring)	Cp_2Mg[f,g] (C_5v ring)	"$CpMgCH_3 \cdot Et_2O$"	"$CpMgCH_3$"
Cyclopentadienyl fundamentals					
ν(CH)	3048	3048 2906	3067 2913	3070 h	3070 h
ν(CC) (ring deformation)	1145	1426 1120	1428 1108	h h	1418
δ(CH)	1009	1003	1004	1006	1001
π(CH)	702	746	779 758	775	770 720

$[(CH_3)_2Be]_n$[d] (D_2h)	$[(CH_3)_2Mg]_n$ (D_2h)	"$CpMgCH_3 \cdot Et_2O$"	"$CpMgCH_3$"	Cp_2Mg[g]
Skeletal vibrations (above 250 cm^{-1})				
567	575	570	575	520
535	440	517	510	435
427	400	409	410	
403	310	310	308	
292				

[a] Throughout the table and the text we have adopted the nomenclature used by Nakamoto (22) to describe the fundamental vibrations of various groups: ν, stretching; δ, in-plane bending or deformation; π, out-of-plane bending; ρ_w, wagging; ρ_r, rocking; ρ_t, twisting. Subscripts "s" or "sym" mean symmetric; "a" or "asym" mean antisymmetric (or asymmetric); "d" means degenerate. The antisymmetric methyl deformation $\delta_a(CH_3)$, is also referred to as the degenerate methyl deformation, $\delta_d(CH_3)$. All frequencies are cited in wave numbers, cm^{-1}.

[b] The formulaes "$CpMgCH_3 \cdot Et_2O$" and "$CpMgCH_3$" where $Cp = C_5H_5$ denote the empirical formula of the materials and are not intended to convey other than the most general structural information.

[c] Reference 23.

[d] References 20, 24 and 25.

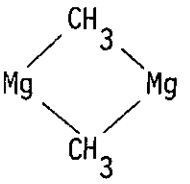
[e] In the gas phase methyl rocking modes have been assigned at 1086, 1032 and 816 cm^{-1}.

[f] References 21 and 22.

[g] Reference 11.

[h] Detection impossible due to other absorptions in this region.

intense bands due to vibrations of a system of methyl bridge bonds. When the bridge bond system is treated as a group with D_2h local symmetry,



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vibrations belonging to the B_{1u}, B_{2u} and B_{3u} irreducible representations are expected to be infrared-active (18-20). Appendix 1 contains the group theory arguments which lead to this conclusion.

Desolvation of "$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$" under mild conditions to yield "$C_5H_5MgCH_3$" has little effect upon the methyl fundamentals or skeletal vibrations. However, there are noticeable changes involving the cyclopentadienyl fundamentals, including reduction of the intensity of the ν(CH) band, which lead to the suggestion that the unexpectedly easy desolvation is facilitated by electronic reorganization in the cyclopentadienyl group.

The stability of solid "$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$" was investigated by thermogravimetric analysis (see Chapter II for details of the experiment). The finely ground sample was placed on the balance in an argon atmosphere. As the furnace was evacuated at 25°, a rapid loss of weight was observed and a condensable gas, $(C_2H_5)_2O$, was evolved as indicated by the shaded area on the extreme left of the pressure plot in Figure 2. After four hours the pressure before and after the liquid nitrogen trap had equilibrated. Heating was begun at a rate of one degree per minute and between approximately 60° and 140° the sample sublimed out of the

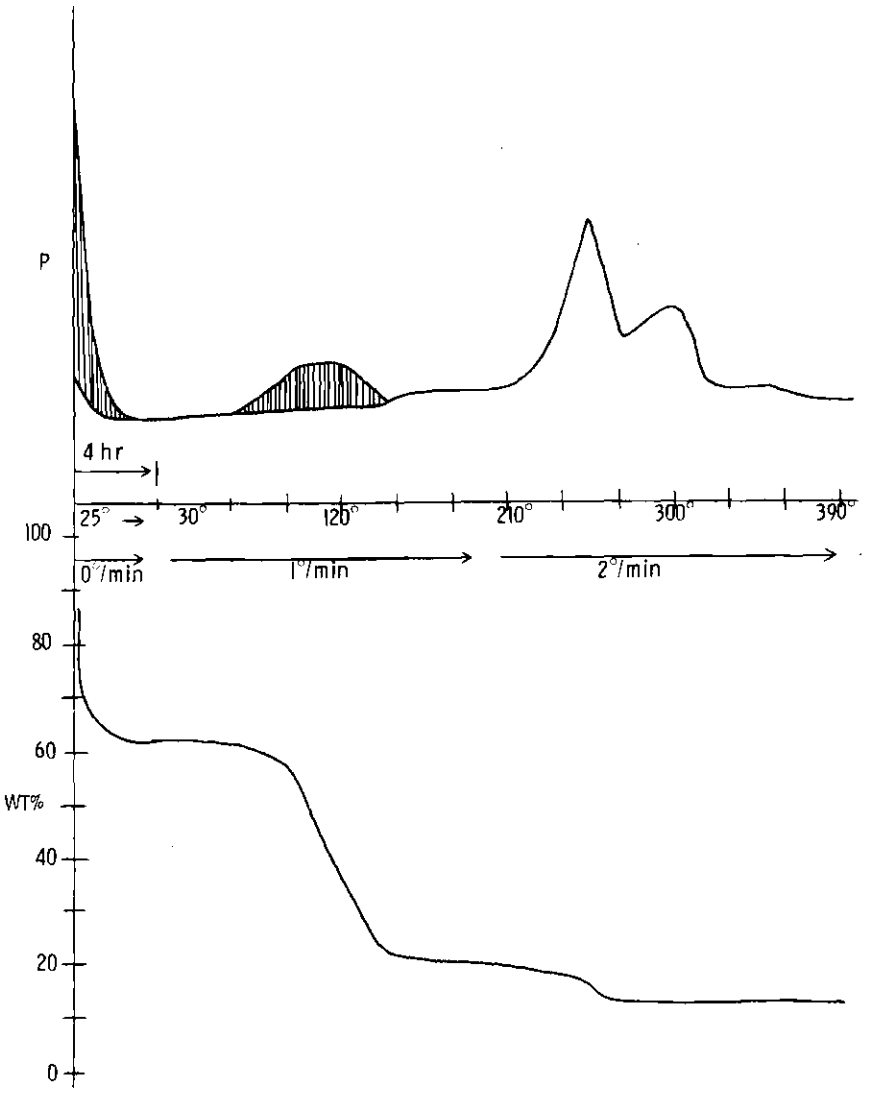


Figure 2. Thermogravimetric Analysis and Differential Pressure Plot of Cyclopentadienylmethylmagnesium Monoetherate

crucible. Sublimation of "$C_5H_5MgCH_3$" is accompanied by substantial disproportionation to $(C_5H_5)_2Mg$ and $(CH_3)_2Mg$. House and co-workers (14) sublimed "$C_5H_5MgCH_3$" into a mass spectrometer and observed that the peak for $[(C_5H_5)_2Mg]^+$ (m/e = 154) was six or seven times as large as the peak for $[C_5H_5MgCH_3]^+$ (m/e = 104). Above 150° only dimethylmagnesium remains in the crucible and, as we have observed for pure, authentic samples of dimethylmagnesium, it decomposes in two steps at 250° and 300° with loss of non-condensable gases. The weight loss ratios are roughly 7 to 1 and may represent the following sequences originally proposed some years ago (27).

$$(CH_3)_2Mg \xrightarrow{250°} "CH_2Mg" + CH_4$$

$$"CH_2Mg" \xrightarrow{300°} "CMg" + H_2$$

The outstanding features of cyclopentadienylmethylmagnesium monoetherate as deduced from the experiments described above are incorporated in the structure proposed in Figure 3.

Solution Phase Studies

In Figure 4, the infrared spectra of the skeletal CH_3-Mg region of solutions of cyclopentadienylmethylmagnesium monoetherate is compared with the solid phase spectrum. Salinger and Mosher (27) have shown that monomeric dimethylmagnesium in diethyl ether or tetrahydrofuran has a single ν(C-Mg) band at approximately 530 cm^{-1}. In concentrated diethyl ether solutions or the solid phase, where dimethylmagnesium exists as methyl bridged polymers, an additional band at 593 cm^{-1} was observed due

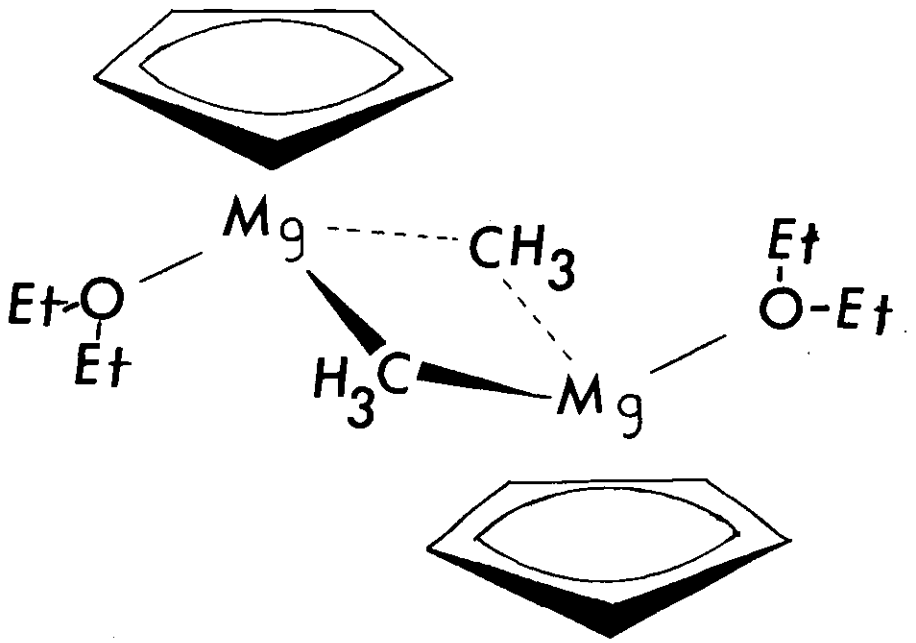


Figure 3. Proposed Structure of
Cyclopentadienylmethylmagnesium Monoetherate

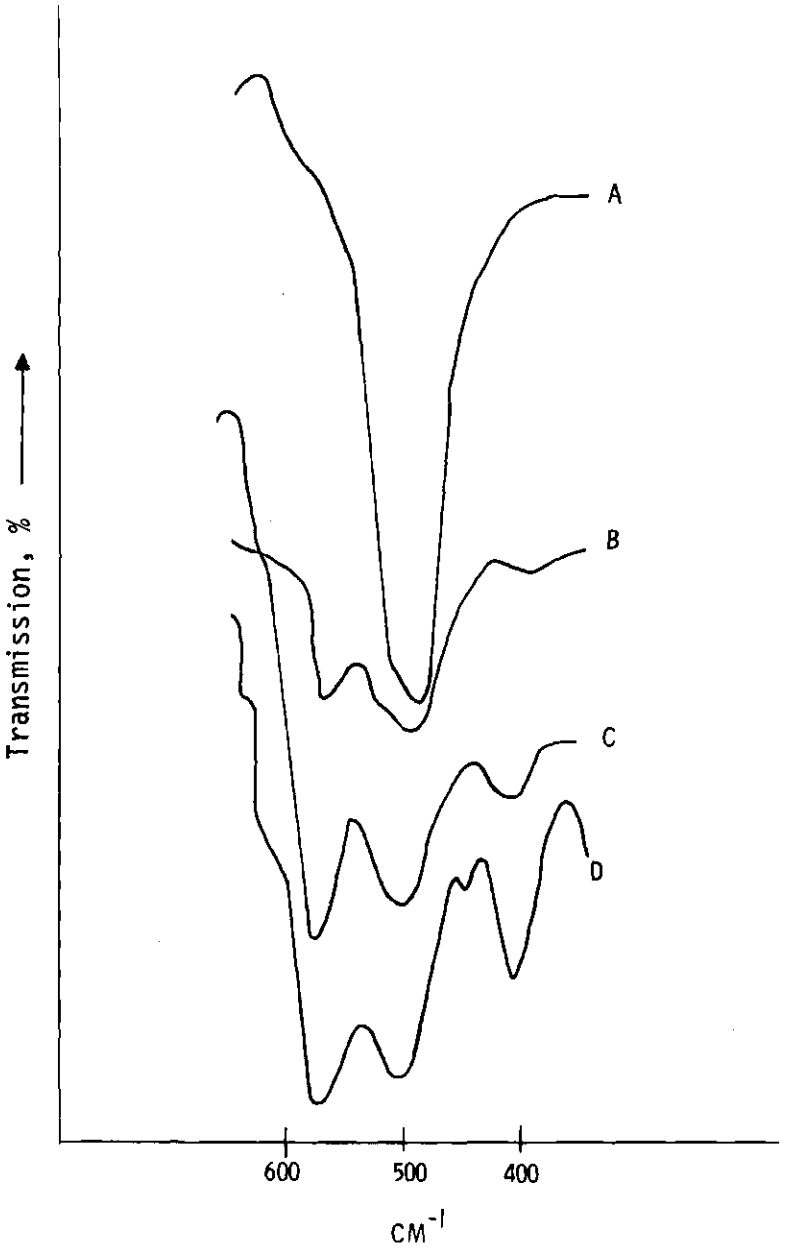


Figure 4. Infrared Spectra of Cyclopentadienylmethylmagnesium Monoetherate (600-400 cm^{-1}) (A) Tetrahydrofuran Solution (B) Diethyl Ether Solution (C) Benzene Solution (D) Solid as Nujol Mull

to the methyl bridge system. A single band was observed in the spectrum of the tetrahydrofuran solution of "$C_5H_5MgCH_3\cdot(C_2H_5)_2O$" at 490 cm^{-1} (spectrum A, Figure 4). In concentrated diethyl ether solution, additional bands at 570, 520 and 400 cm^{-1} appear though the band at 490 cm^{-1} is still predominant (spectrum B, Figure 4). In benzene (spectrum C, Figure 4) the bands at 575, 520 and 400 cm^{-1} are more intense and the spectrum is very similar to the solid phase spectrum (spectrum D, Figure 4). Thus, the infrared spectra suggest that cyclopentadienylmethylmagnesium monoetherate dissolves in benzene with retention of the methyl bridge system deduced in the solid phase structure. On the other hand, polar solvents, such as diethyl ether and particularly tetrahydrofuran, cleave the bridge bonds according to Equilibrium 1.

$$[C_5H_5MgCH_3\cdot(C_2H_5)_2O]_2 + 2\ (C_2H_5)_2O \rightleftharpoons 2\ C_5H_5MgCH_3\cdot 2(C_2H_5)_2O \quad (1)$$

Ebullioscopic molecular association studies in ether support this conclusion since the apparent molecular weight which is 1.70 times the monomeric molecular weight near saturation (0.111 m) decreases with dilution, approaching the monomeric molecular weight at infinite dilution. In tetrahydrofuran, the ether is apparently completely replaced by tetrahydrofuran and Equilibrium 1 is driven far to the right. It has been reported that "$C_5H_5MgCH_3$" is monomeric in tetrahydrofuran over a wide concentration range (14). It is likely that disolvated monomers are the predominant species in tetrahydrofuran solution.

Two lines of evidence suggest that ether partially dissociates from the methyl bridged dimer of cyclopentadienylmethylmagnesium monoetherate in benzene solution according to Equilibrium 2.

$$[C_5H_5MgCH_3\cdot(C_2H_5)_2O]_2 \rightleftharpoons (C_5H_5MgCH_3)_2\cdot(C_2H_5)_2O + (C_2H_5)_2O \qquad (2)$$

The apparent molecular weight of cyclopentadienylmethylmagnesium monoetherate as determined by cryoscopy in benzene is 1.26 to 1.29 times that of the solvated monomer in the concentration range 0.100-0.238 m. This result by itself does not distinguish between Equilibria 2 and 3,

$$[C_5H_5MgCH_3\cdot(C_2H_5)_2O]_2 \rightleftharpoons 2\ C_5H_5MgCH_3\cdot(C_2H_5)_2O \qquad (3)$$

although the infrared spectra in Figure 4 have revealed that the methyl bridge bonds remain largely intact in benzene solution. Direct evidence for dissociation of ether as suggested by Equilibrium 2 comes from the infrared spectra of cyclopentadienylmethylmagnesium monoetherate in benzene between 1200 and 1000 cm^{-1} as shown in Figure 5. In addition to $\delta_s(CH_3)$ at 1190 cm^{-1} and $\delta(C_5H_5)$ at 1005 cm^{-1}, there are five ether skeletal vibrations in this region near 1145, 1115, 1087, 1045 and 1025 cm^{-1} (29). The intensities of these bands depend upon the conformation of the ether molecules (18, 29-33). For free diethyl ether diluted with benzene these bands are broad and overlap due to the presence of numerous slightly different conformers and the band at 1115 cm^{-1} tends to be the most intense, (spectrum C, Figure 5). In the solid phase spectrum of "$C_5H_5MgCH_3\cdot(C_2H_5)_2O$", the ether bands are sharp with characteristic intensities since the ether molecules are constrained to a preferred conformation (spectrum A, Figure 5). The ether spectrum for cyclopentadienylmethylmagnesium monoetherate in benzene (spectrum B, Figure 5) consists of five moderately sharp bands superimposed on a broad envelope of absorption. The envelope absorption is assigned to

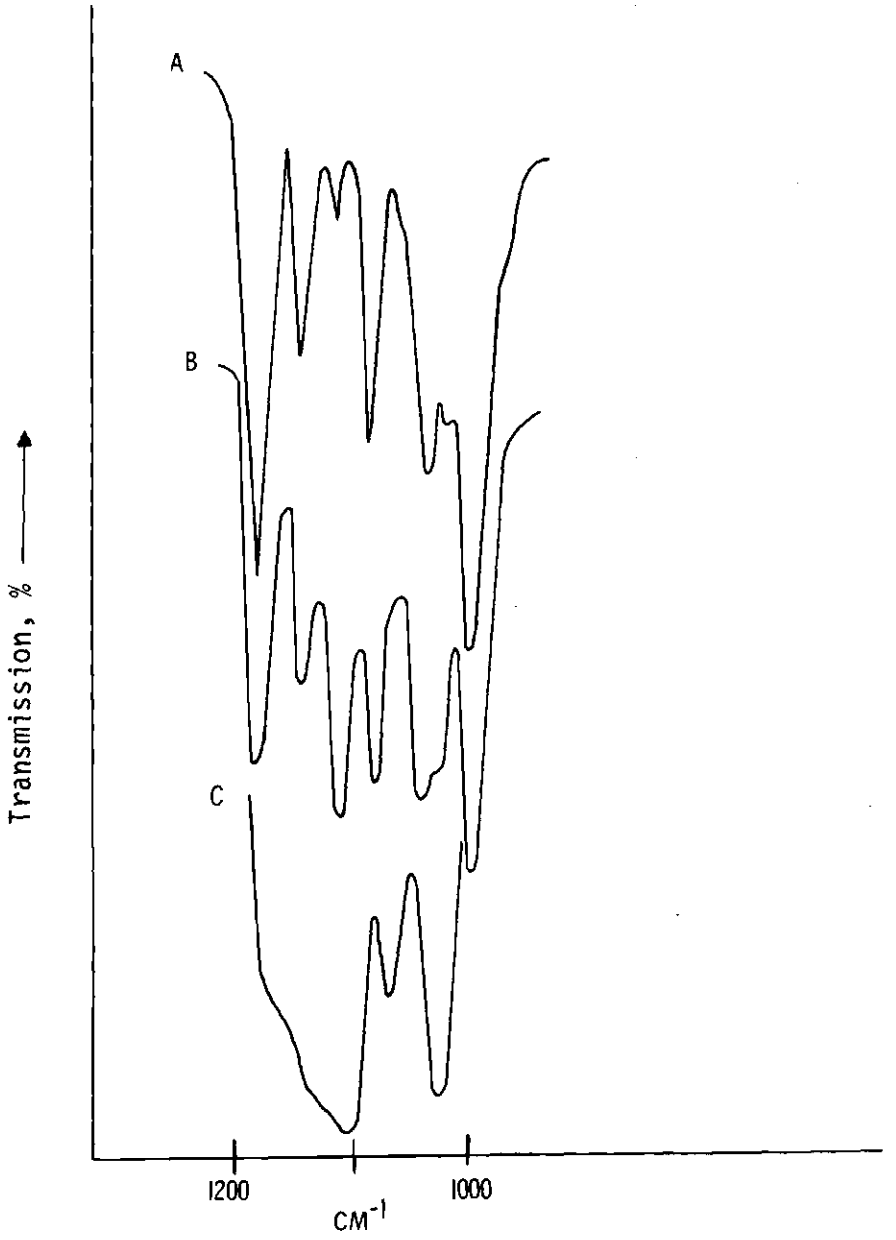


Figure 5. Infrared Spectra of Coordinated and Free Diethyl Ether
(A) Solid Cyclopentadienylmethylmagnesium as Nujol Mull
(B) Benzene Solution of Cyclopentadienylmethylmagnesium Monoetherate (C) Benzene Solution of Diethyl Ether

free ether molecules, while the sharper peaks are assigned to coordinated ether. Comparing the relative intensities of the sharp peaks in spectra A and B of Figure 5 suggests that the preferred conformation of the coordinated ether molecules is different in the solid and solution phases.

As seen in Table 2, the proton magnetic resonance signal for the C_5H_5 group of "$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$" is sensitive to the solvent employed as is the signal for $(C_5H_5)_2Mg$. Temperatures as low as -80°C have little if any effect upon the C_5H_5 signal of these compounds in the stated solvents. The methyl proton resonance of "$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$" is also solvent sensitive as would be expected from Equilibria 1 and 2 (34). The strong anisotropic field of the C_5H_5 group can potentially shield or deshield the methyl group depending upon the relative positions of the two groups. In tetrahydrofuran where the principal species in solution is the solvated monomer of "$C_5H_5MgCH_3$", the methyl group appears to fall within the shielding cone of the C_5H_5 group though it is not necessarily on the fivefold axis of the ring as previously suggested (14). In view of Equilibria 1 and 2, the interaction of anisotropic and local diamagnetic electron shielding upon the observed methyl proton chemical shifts in diethyl ether, benzene or toluene is not easily predicted. Thus, rationalization of the observed chemical shifts is somewhat superficial. Nonetheless, the low field position of the methyl-chemical shift in benzene or toluene solution is consistent with the methyl bridged dimer which has been proposed. There is little temperature effect upon the methyl signal in tetrahydrofuran or toluene at temperatures as low as -80° but in diethyl ether three signals were

Table 2. PMR Spectra of Delocalized Cyclopentadiene Derivatives

Compound	Solvent	Chemical Shifts (τ)[a] C_5H_5	CH_3
"$C_5H_5MgCH_3 \cdot (C_2H_5)_2O$"	Tetrahydrofuran	4.13 (4.13)[b]	12.13 (12.10)[b]
	Diethyl Ether	4.03	11.70
	Benzene (Toluene)	3.67	11.17
$(C_5H_5)_2Mg$	Tetrahydrofuran	4.13 (4.13)[b]	
	Diethyl Ether	3.99 (3.99)[b]	
	Benzene (Toluene)	3.85	
$(CH_3)_2Mg$[c]	Diethyl Ether		11.00 - 11.40[c] (bridging)
			11.60 - 11.75[c] (terminal monomer)
	Tetrahydrofuran		11.80 - 11.85[c] (monomer)

[a]Benzene internal standard (2.70 τ)

[b]From Reference 14

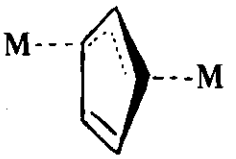
[c]From Reference 34

resolved (11.66, 11.88 and 12.02 τ) at -65°. The highest field signal is the most intense and is probably due to a solvated monomer of "$C_5H_5MgCH_3$". The lower field signals appear to be due to less soluble components since the intensity of the signals decreases with time.

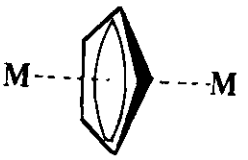
CHAPTER IV

CONCLUSIONS

The major conclusions concerning the solid state structure of cyclopentadienylmethylmagnesium monoetherate as discussed in Chapter III are embodied in Figure 3. The structure of the unsolvated cyclopentadienylmethylmagnesium appears to retain the methyl bridge bond system. The bonding of the cyclopentadienyl group apparently adjusts during desolvation to maintain coordinate saturation of the magnesium atom. Since the material disproportionates to $(C_5H_5)_2Mg$ and $(CH_3)_2Mg$ upon heating to 100°, there must be intermolecular migration of the C_5H_5 group in the solid phase. This migration may take place via a C_5H_5 bridge. There are several possibilities for a bridging configuration. The structures of $(C_5H_5)_3In$ (3) and $(C_5H_5)_3Sc$ (4) have cyclopentadienyl bridges with metal-carbon contacts at the 1 and 3 positions of the ring.



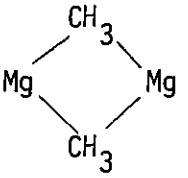
In the case of cyclopentadienyldimethylaluminum, a different type of bridging has been proposed which involves all the positions on the ring equally (5,6).



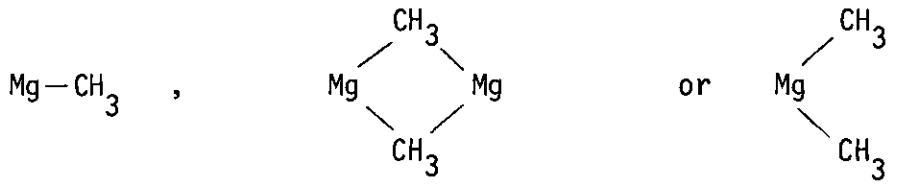
Very recently, Atwood and Smith (35) have found that bis(indenyl)magnesium has a very complicated solid phase structure and they argue that crystal packing forces determine the molecular structure in the absence of overriding bonding preferences. In the case of dicyclopentadienylmagnesium, the sandwich structure (similar to ferrocene) is simultaneously compatible with the ionic bonding model and crystal packing forces. In the case of bis(indenyl)magnesium, the crystal packing forces determine the structure because the bonding forces are flexible (i.e., not restricted to nor dependent on a particular geometry). It seems likely that cyclopentadienylmethylmagnesium (unsolvated) has a complex structure in which crystal packing forces are more important than the precise geometry of the cyclopentadienylmagnesium interaction as long as magnesium can achieve a reasonable degree of coordinate saturation. A structure with bridging C_5H_5 groups would account for the disproportionation to $(C_5H_5)_2Mg$ and $(CH_3)_2Mg$.

The interpretation of the infrared skeletal vibrations involving the methyl-magnesium bond in cyclopentadienylmethylmagnesium can be pursued on two levels. On the most elementary level, it is clear that absorptions in the 600-400 cm^{-1} region of the spectra of methylmagnesium compounds are mainly due to vibrations of the carbon-magnesium bond. The absorptions are characteristically broad and relatively intense. The infrared spectra in the 600 to 300 cm^{-1} region of

dimethylmagnesium, cyclopentadienylmethylmagnesium and similar compounds in solution change with solvent and concentration. Characteristically in situations where physical evidence (PMR, molecular association or crystallography) suggests that there are bridge bonds of the D_2h type



present, a strong IR absorption at 600 to 550 cm^{-1} is observed with additional bands in the 550 to 300 cm^{-1} region which also appear to be due to C-Mg vibrations. In cases where evidence supports the existance of only simple carbon-magnesium single bonds, the skeletal regions of the IR spectra are typically relatively simple with a strong band at 530-480 cm^{-1} and no bands above 550 cm^{-1} attributable to C-Mg vibrations. In cases where both bridging and terminal linkages are expected, there are bands in all the regions cited above (28). From these results alone, a strong argument by analogy can be constructed which suggests that a band in the 600-550 cm^{-1} region of the spectra of a methylmagnesium compound, such as cyclopentadienylmethylmagnesium in the solid phase, is due to the presence of the D_2h methyl bridge system. On a slightly more refined level, the principles of group theory when applied to structures such as



allow the prediction of the number and symmetry of infrared active vibrations which may be expected for each structure provided these vibrations do not couple strongly with other molecular vibrations. These arguments are discussed in Appendix 1 and for brevity their results will not be recapitulated here.

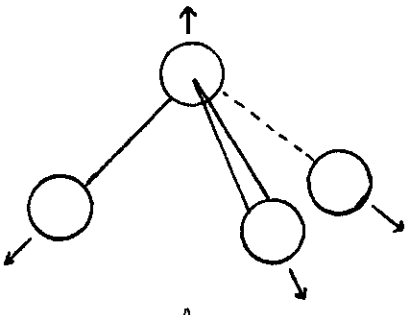
Infrared spectroscopy is also used in Chapter III to distinguish between coordinated and free diethyl ether molecules. The distinction is based upon the fact that conformationally labile molecules adopt many slightly different conformations when free, while coordinated molecules are constrained to a few preferred conformations. The C-O and C-C region (1200 to 1000 cm^{-1}) of the spectrum is most sensitive to these changes in structure.

APPENDIX I

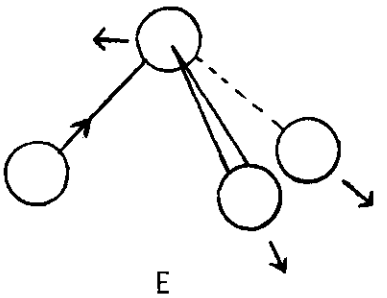
INFRARED SPECTRA OF METHYL-MAGNESIUM COMPOUNDS

Infrared spectroscopy is a very useful tool for qualitative structure determination. Nakamoto (22) has provided the most extensive discussion of the infrared spectra of organometallic compounds, but the discussion is limited to interpretation and analysis of characteristic group frequencies for organic groups bound to metals. Relatively little work concerning the use of skeletal C-Mg vibrations for structure elucidation has been published. The purpose of this appendix is to review the published results and collate them into a summary of the characteristic metnyl group frequencies and to examine the possible use of skeletal C-Mg vibrations to determine structural units in methyl-magnesium compounds.

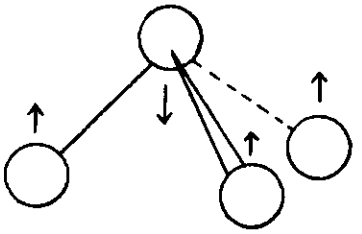
The methyl group has C_3v symmetry and such a system has been treated in detail by Cotton (36). The genuine internal vibrations are $2A_1 + 2E$. All four of these vibrations are infrared and Raman active.



A_1
(symmetric stretch)

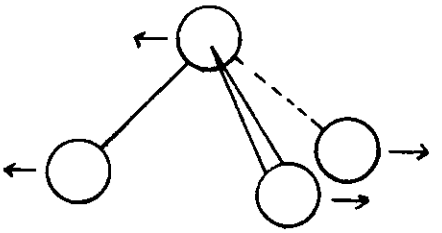


E
(asymmetric stretch
degenerate pair)



A_1

(symmetric deformation)



E

(asymmetric deformation degenerate pair)

In addition to these internal vibrations, methyl rocking modes can be described in which the CH_3 group "rocks" as a single unit on the carbon-metal bond. In this vibration the center of mass of the CH_3 group does not move but the group "rocks" such that the threefold axis is not always directed at the metal. This vibration is distinct from an X-M-CH_3 bending vibration where the $XMCH_3$ angle changes and the center of mass of the CH_3 group moves. Thus there are five vibrations involving the methyl group which may be used to establish its presence.

These vibrations are sensitive to the polarity of the carbon-metal bond but they are not directly related to the type of bonding. As the carbon-metal bond becomes more polar, negative charge is shifted onto the carbon atom and it is stabilized by localization in a carbon orbital with a large amount of s character. The carbon-hydrogen bonds then must be formed from carbon orbitals with large amounts of p character (small amounts of s character). This trend in hybridization results in a weakening of the C-H bond (i.e., the C-H stretching force constant decreases as the p character of the carbon atomic orbital increases (19)).

Even though the C-H stretching vibrations usually give rise to low intensity (weak or medium) infrared absorptions, these bands can be very useful for characterization of methyl compounds of the electropositive metals because the low force constants of the C-H bonds cause the C-H stretching absorptions to occur at rather low frequency (wave number), well separated from the C-H absorptions of other organic groups which might be present. In ordinary alkanes the asymmetric and symmetric C-H stretches of the methyl group occur at approximately 2960 and 2870 cm^{-1} respectively while these bands are observed near 2850 and 2780 cm^{-1} in methyl-lithium and methyl-magnesium compounds.

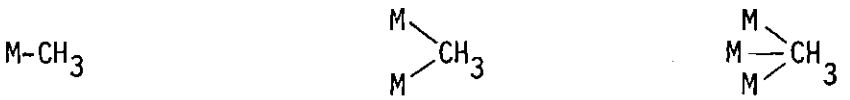
The degenerate asymmetric methyl deformation gives rise to a band that is characteristically very weak and frequently not observed for methyl groups bound to electropositive metals. The band is expected in the region around 1400 cm^{-1}.

The symmetric methyl deformation absorption is usually a strong, sharp band which is sensitive to the electronegativity of the metal. The absorption moves to lower frequency as the metal becomes more electropositive. The band usually occurs between 1300 and 1100 cm^{-1} and it is often split into two components 5 to 10 cm^{-1} apart. For methyl groups bound to magnesium the symmetric methyl deformation is usually observed as a band between 1200 and 1175 cm^{-1}.

The bands for the methyl rocking modes usually occur between 950 and 700 cm^{-1}. Like the bands for the symmetric methyl deformation, it tends toward lower frequency as the metal to which the methyl group is bound becomes more electropositive. For methyl groups bound to magnesium

the rocking mode(s) usually can be observed between 800 and 700 cm^{-1}, but the band(s) are often not easily distinguished from other bands in this region if the molecule is complex.

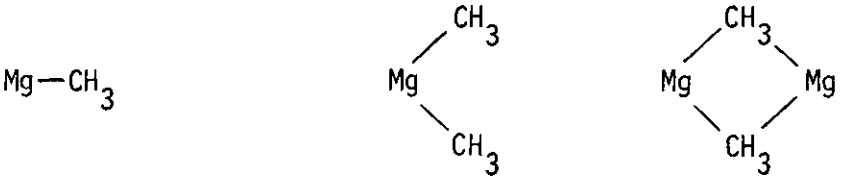
The C-H stretch and symmetric deformation absorptions are the most useful methyl fundamentals for characterization. However, as mentioned above, the methyl fundamentals are not diagnostic of the type of bonding of the methyl group to the metal. It is of considerable interest to establish infrared criteria for distinguishing between some of the more common types of methyl-metal bonds:



The establishment of characteristic group frequencies requires that substructures can be defined which vibrate as a single unit and vibrate independent of the rest of the molecule. In the case of the alkylboron hydrides, it has been possible to establish characteristic group frequencies for various substructures with different types of boron-hydrogen bonds. This result is due to the fact that hydrogen is so much less massive than boron that the boron "damps out" other vibrations. That is, in the vibrations which involve boron and hydrogen atoms, displacement of the boron atoms is small relative to displacement of the hydrogen atoms. To a first approximation such a vibration can be treated solely in terms of hydrogen displacement relative to the rigid framework of the molecule in which the boron is fixed. The situation is more complex in the case of carbon-magnesium bonds since sizable

displacements of magnesium must be considered in any vibration. Thus, a meaningful interpretation of the skeletal methyl-magnesium vibrations requires a judicious compromise of rigor and simplicity. The problem is to approximate the molecular vibrations as the sum of substructure vibrations where the substructures involve as few atoms as possible without subdividing the molecular vibrations beyond a realistic point. The value of defining substructures as simply as possible is that the analysis would become more readily transferable from one compound to another.

Three substructures which show promise of being assigned group frequencies which are relatively independent of the molecule in which they are found are shown below. It is assumed that any additional



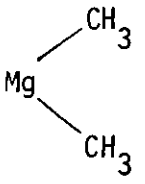
bonds to magnesium involve greatly different force constants and/or the masses of the pendent atoms are different from carbon. As pointed out by Harmony (37):

> In simple terms, they [characteristic frequencies for groups of heavy atoms] occur when the group in question has a force constant which is considerably different from that of its neighboring bonds, even though the atoms in question are of approximately the same mass; or they occur if the force constants are similar and the masses quite different. . . . Thus the carbonyl stretch is distinct in formaldehyde (H_2CO) and also in acetaldehyde (CH_3CHO). In the former case the carbonyl group masses are much different from those of the adjacent atoms, but in the latter the adjacent atom is heavy. Nevertheless, the carbonyl frequency is distinct because the C=O force constant is much larger than that of the C-C bond.

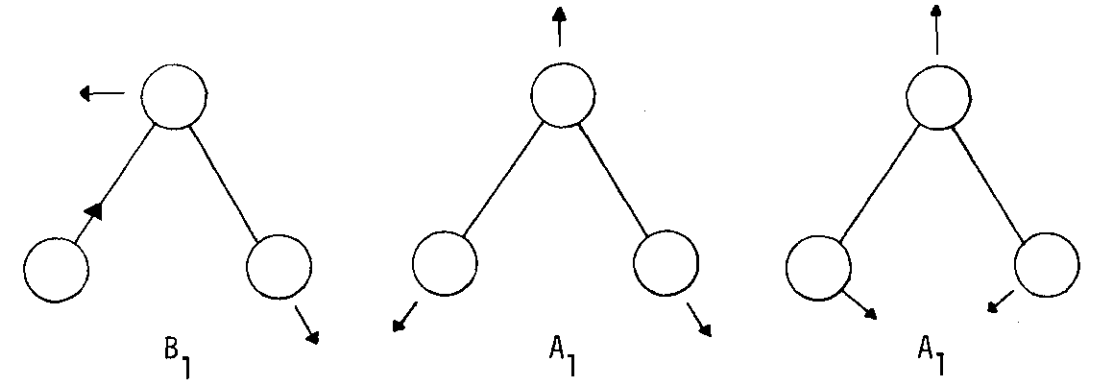
Ignoring the hydrogen atoms (the C-H vibrations have already been considered in the methyl fundamentals), these substructures have C_∞, C_2v and D_2h symmetry respectively.

The simple two-center two-electron C-Mg bond with C_∞ symmetry can only give rise to one vibration, namely the change in internal coordinates corresponding to a change in the bond length. According to selection rules, this vibration is both infrared and Raman active. Thus it should be possible to identify the C-Mg stretching vibration in a number of compounds such as solvates of alkylmagnesium halides. Such assignments have usually been made in the 550 to 450 cm^{-1} region of the infrared spectrum (28).

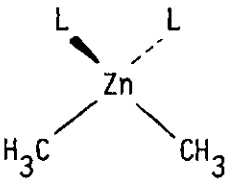
Whereas in a compound of the type $CH_3MgX \cdot 2S$, the methyl-magnesium bond vibration can probably be treated as a group frequency because the other bonds to magnesium are so different in terms of both force constants and masses of the pendent atoms, the methyl-magnesium bonds in a solvated dimethylmagnesium monomer $(CH_3)_2Mg \cdot 2S$ are probably best treated by considering the



portion of the molecule as a bent triatomic molecule with C_2v local symmetry. Such a group would give rise to three infrared active vibrations, 2 A_1 and B_1 (38).



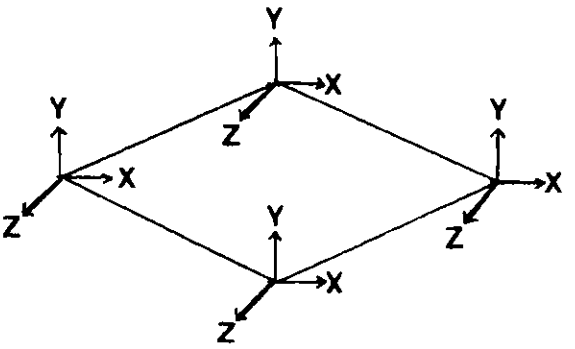
(asymmetric stretch) (symmetric stretch) (bend)



No such assignments have yet been made for dimethylmagnesium, but in the case of dimethylzinc complexes (solvates), Evans and Wharf (39) have identified both the symmetric and asymmetric carbon-zinc stretching frequencies. For the pyridine, bipyridine and tetramethylethylenediamine complexes the asymmetric stretch is assigned to a band at 510 $\pm$ 4 cm^{-1} and the symmetric stretch is assigned to a band at 464 $\pm$ 4 cm^{-1}. In principle, these vibrations must involve all the atoms in each complex, but the observation that these bands do not change appreciably with different ligands indicates that the vibrations are adequately approximated by considering only the displacements of the zinc atom and methyl groups.

The four-center electron-deficient bridge bond system with D_2h local symmetry should have six normal vibrations. With the aid of group theory the symmetry of these vibrations can be deduced. Since there is

no easily available reference for the group theory arguments, they are outlined in the following paragraphs. Basically the independent atomic coordinates will be operated on by the operations of the D_2h group to yield a total representation of the group. The total representation will be decomposed to a sum of irreducible representations. From this sum, the translational and rotational degrees of freedom will be eliminated to leave only the genuine vibrational modes. Finally, selection rules will be consulted to determine whether the normal mode will actually give rise to absorption.



In the coordinate system shown above, the x,y-plane corresponds to the plane of the D_2h ring. The z-axis is out of the plane of the ring. Each operation of the D_2h symmetry group is applied to the set of coordinates. Each coordinate which transforms into itself under an operation contributes +1, each coordinate which transforms into minus itself contributes -1, and each which transforms into some other coordinate contributes 0 to the total representation. (See Table 3.) As examples, the identity operation (E) transforms each of the twelve coordinates

Table 3. D_2h Character Table

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(x,y)$	$\sigma(x,z)$	$\sigma(y,z)$	
A_g	1	1	1	1	1	1	1	1	
B_{1g}	1	1	-1	-1	1	1	-1	-1	Rz
B_{2g}	1	-1	1	-1	1	-1	1	-1	Ry
B_{3g}	1	-1	-1	1	1	-1	-1	1	Rx
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x

into itself; the twofold rotation about the z-axis ($C_2(z)$) moves every coordinate into some other coordinate; and reflection in the x,y-plane ($\sigma(x,y)$) transforms eight of the coordinates (the x and y coordinates) into themselves and four of the coordinates (the z coordinates) into minus themselves for a net of four coordinates transformed into themselves. Similar application of all eight operations of the D_2h group gives the total representation (Γ_{tot}).

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(x,y)$	$\sigma(x,z)$	$\sigma(y,z)$
Γ_{tot}	12	0	-2	-2	0	4	2	2

The total representation can now be decomposed into the irreducible representations from which it is formed.

$$\Gamma_{tot} = \sum \Gamma_{irrd}$$

This procedure is basically trial-and-error (though the number of trials is limited to the number of irreducible representations) using the equation

$$a_i = \frac{1}{h} \sum_R \chi(R)\, \chi_i(R)$$

where a_i is the number of times the ith irreducible representation appears in the sum, h is the order of the group, $\chi(R)$ is the character of the total representation for the Rth operation, and $\chi_i(R)$ is the character of the ith irreducible representation for the Rth operation. The sum includes all operations in the point group. For example, the

number of times the A_g irreducible representation is contained in the total (reducible) representation of the group is given by substitution into the following equation.

$$a_{A_g} = \frac{1}{8}\left[(12)(1) + (0)(1) + (-2)(1) + (-2)(1) + (0)(1) + (4)(1) + (2)(1) + (2)(1)\right]$$

$$= \frac{1}{8}\left[12 - 2 - 2 + 4 + 2 + 2\right] = \frac{16}{8} = 2$$

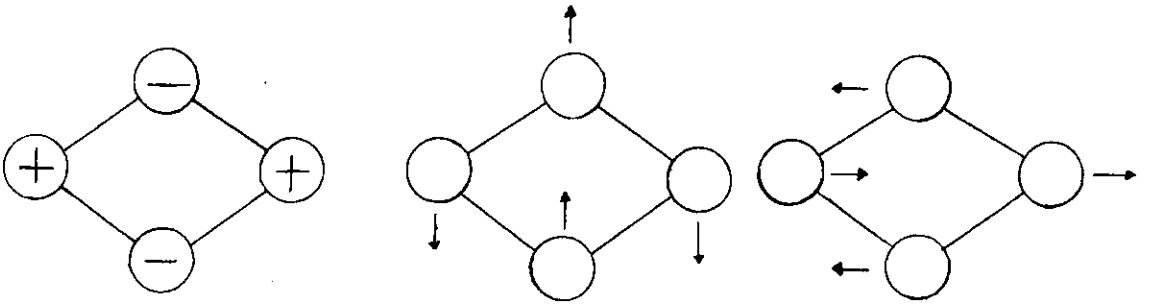
By repeating the above procedure the total representation is found to be composed as shown below.

$$\Gamma_{tot} = 2\,A_g + 2\,B_{1g} + B_{2g} + B_{3g} + 2\,B_{1u} + 2\,B_{2u} + 2\,B_{3u}$$

Examination of the D_2h character table (Table 3) shows that the translations of the group have B_{1u}, B_{2u} and B_{3u} symmetry and the rotations have B_{1g}, B_{2g} and B_{3g} symmetry. Subtracting these from the total representation gives the genuine vibrational modes of the D_2h system.

$$\Gamma_{genuine} = 2\,A_{1g} + B_{1g} + B_{1u} + B_{2u} + B_{3u}$$

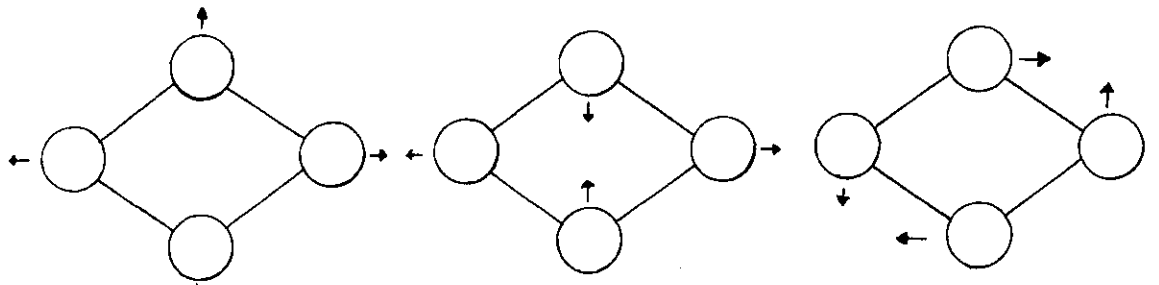
In order for a vibration to be infrared active, it must have the same symmetry properties as one of the coordinate axes. The B_{1u}, B_{2u} and B_{3u} vibrations transform like z, y and x respectively and should be infrared active. However, they are not Raman active because they do not



B_{1u} B_{2u} B_{3u}

out of plane in plane

transform like a product or sum of products of two of the coordinates (e.g., x^2, xy, x^2-y^2). The 2 A_{1g} and B_{1g} vibrations are Raman active.



A_{1g} A_{1g} B_{1g}

This result is a good example of the general rule that molecules with an inversion center will have mutually exclusive infrared and Raman spectra. All infrared active bands are ungerade (u) and all Raman active bands are gerade (g).

The three bands expected for the D_2h methyl bridge system should fall in the 600-200 cm^{-1} region of the infrared spectrum. The assignment of symmetry to the specific observed bands is more difficult and requires detailed force constant calculations. In the examples which

have been studied, the three infrared bands occur in the ranges 600 to 550 cm^{-1}, 550 to 450 cm^{-1} and 450 to 350 cm^{-1}. The band at 600 to 550 cm^{-1} is the most characteristic since it does not seem to be affected greatly by changes in the other parts of the molecule and it is observed in a region which is at higher frequency than most other types of C-Mg vibrations.

One notable example where the group frequency arguments do not apply is the case of polymeric dimethylmagnesium which is composed of many adjacent methyl bridge systems. Obviously, force constants and atomic masses within adjacent bridges are similar and the molecular vibrations cannot be localized into individual bridges. Thus, it is not surprising that the spectra of compounds with "isolated" methyl bridge systems are different from those with "adjacent" methyl bridge systems.

APPENDIX 2

MOLECULAR ASSOCIATION STUDIES

Cryoscopic Data for "$(C_5H_5)_2Mg$" in Benzene

T_{fp}	ΔT_{fp}	Benzene (gr)	$(C_5H_5)_2Mg$ (gr)
5.755	0	41.845	0
5.265	0.490	51.8900	0.7858
4.920	0.835	62.1912	1.5917
4.700	1.055	70.6061	2.2496

Concentration (m)	Molecular Weight[a]	i-value[b]
0.098	151	0.98
0.166	150	0.97
0.207	148	0.96

k_{fp} = 4.90 deg·kg·mole^{-1}

[a]Molecular weight "$(C_5H_5)_2Mg$" is 154.

[b]Estimated experimental uncertainty is ± 5%.

Cryoscopic Data for "$C_5H_5MgCH_3 \cdot (C_2H_3)_2O$" in Benzene

T_{fp}	ΔT_{fp}	Benzene (gr)	"$C_5H_5MgCH_3 \cdot (C_2H_3)_2O$" (gr)
5.755	0	41.900	0
5.365	0.390	51.125	0.9138
5.105	0.650	60.109	1.8037
4.855	0.900	73.287	3.1091

Concentration (m)	Molecular Weight[a]	i-value[b]
0.100	225	1.26
0.168	226	1.27
0.238	231	1.29

$k_{fp} = 4.90$ deg·kg·mole^{-1}

[a]Molecular weight "$C_5H_5MgCH_3 \cdot (C_2H_3)_2O$" is 178.

[b]Estimated experimental uncertainty is $\pm$ 5%.

Ebullioscopic Data for "$C_5H_5MgCH_3 \cdot (C_2H_3)_2O$" in Diethyl Ether

T_{bp}	ΔT_{bp}	$(C_2H_3)_2O$ (gr)	"$C_5H_5MgCH_3 \cdot (C_2H_3)_2O$" (gr)
0.990	0	65	0
1.123	0.133	58.667	1.184
1.105	0.115	75.880	1.184
1.095	0.105	89.469	1.184

Concentration (m)	i-value[a]
0.111	1.70
0.0874	1.52
0.0741	1.42

k_{bp} = 2.01 deg·kg·mole^{-1}

[a]Estimated experimental uncertainty is ± 10%.

LITERATURE CITED*

(1) G. E. Coates, M. L. H. Green and K. Wade, "Organometallic Compounds, Vol. II, The Transition Elements", Third Ed., Methuen & Company, London, 1967, pp. 90-164.

(2) R. Lucas, M. L. H. Green, R. Forder and K. Prout, J. Chem. Soc., Chem. Comm., 97 (1973).

(3) F. W. B. Einstein, M. M. Gilbert and D. G. Tuck, Inorg. Chem., 11, 2832 (1972).

(4) J. L. Atwood and K. D. Smith, J. Amer. Chem. Soc., 95, 1488 (1973).

(5) A. Haaland and J. Weidlein, J. Organometal. Chem., 40, 29 (1972).

(6) D. A. Drew and A. Haaland, J. Chem. Soc., Chem. Comm., 1300 (1972).

(7) G. Wilkinson, F. A. Cotton and J. M. Birmingham, J. Inorg. and Nuc. Chem., 2, 95 (1956).

(8) W. T. Ford, J. Organometal. Chem., 32, 27 (1971).

(9) S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard and C. F. Pygall, J. Chem. Soc. Faraday II, 68, 1847 (1972).

(10) F. A. Cotton and L. T. Reynolds, J. Amer. Chem. Soc., 80, 269 (1958).

(11) E. R. Lippincott, J. Xavier and D. Steele, J. Amer. Chem. Soc., 83, 2262 (1961).

(12) E. Weiss and E. O. Fischer, Z. Anorg. Alg. Chem., 284, 69 (1956).

(13) C. Johnson, J. Toney and G. D. Stucky, J. Organometal. Chem., 40, C11 (1972).

(14) H. O. House, R. A. Latham and G. M. Whitesides, J. Org. Chem., 32, 2481 (1967).

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*Journal title abbreviations used are listed in "List of Periodicals", Chemical Abstracts, (1961).

(15) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, John Wiley and Sons, New York, N. Y., 1967, pp. 181-182.

(16) E. C. Ashby and J. J. Watkins, Inorg. Chem., 12, 2493 (1973).

(17) F. W. Walker and E. C. Ashby, J. Chem. Ed., 45, 654 (1968).

(18) T. Holm, Acta. Chem. Scand., 19, 1819 (1965).

(19) P. Krohmer and J. Goubeau, Z. Anorg. Alg. Chem., 369, 238 (1969).

(20) G. E. Coates, M. L. H. Green and K. Wade, "Organometallic Compounds, Vol. I, The Main Group Elements", Third Ed., Methuen & Company, London, 1967, p. 105.

(21) H. P. Fritz, Adv. Organometal. Chem., 1, 239 (1964).

(22) K. Nakamoto, "Characterization of Organometallic Compounds, Part I", M. Tsutsui, Ed., Interscience, New York, N. Y., 1969, pp. 73-135.

(23) R. West and W. Glaze, J. Amer. Chem. Soc., 83, 3590 (1961).

(24) J. Goubeau and K. Walter, Z. Anorg. Alg. Chem., 322, 58 (1963).

(25) N. A. Bell and G. E. Coates, cited in G. E. Coates, M. L. H. Green and K. Wade, "Organometallic Compounds, Vol. I, The Main Group Elements", Third Ed., Methuen & Company, London, 1968, p. 105.

(26) E. Maslowsky, Jr. and K. Nakamoto, Inorg. Chem., 8, 1108 (1969).

(27) K. Ziegler, K. Nagel and M. Patheiger, Z. Anorg. Alg. Chem., 282 (1955).

(28) R. M. Salinger and H. S. Mosher, J. Amer. Chem. Soc., 86, 1782 (1964).

(29) M. Auram and G. D. Mateescu, "Infrared Spectroscopy Applications in Organic Chemistry", translated by L. Birladeanu, Wiley Inter-Science, New York, N. Y., 1972, p. 262.

(30) R. Hameline and S. Hayes, Comp. Rend., 252, 1616 (1961).

(31) A. E. Shirk and D. F. Shriver, J. Amer. Chem. Soc., 95, 5904 (1973).

(32) H. Wieser, W. G. Laidlaw, P. J. Krueger and H. Fuhrer, Spectrochim. Acta., Part A, 26, 1349 (1970).

(33) H. Wieser and P. J. Krueger, Spectrochim. Acta., Part A, 26, 1349 (1970).

(34) G. E. Parris and E. C. Ashby, J. Amer. Chem. Soc., 93, 1206 (1971).

(35) J. L. Atwood and K. D. Smith, J. Amer. Chem. Soc., 96, 994 (1974).

(36) F. A. Cotton, "Chemical Applications of Group Theory", Second Ed., Wiley Interscience, New York, N. Y., 1971, pp. 295-339.

(37) M. D. Harmony, "Introduction to Molecular Energies and Spectra", Holt, Rinehart and Winston, Inc., New York, N. Y., 1972, p. 310.

(38) M. D. Harmony, "Introduction to Molecular Energies and Spectra", Holt, Rinehart and Winston, Inc., New York, N. Y., 1972, P. 250.

(39) D. F. Evans and I. Wharf, J. Chem. Soc. (A), 783 (1965).

PART III

SOLUTION COMPOSITION AND INTERCONVERSION OF VARIOUS FORMS OF ALKOXY(METHYL)MAGNESIUM REAGENTS

CHAPTER I

INTRODUCTION

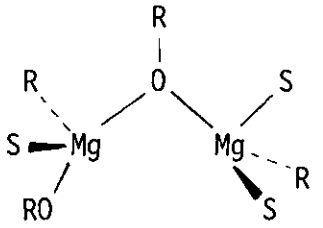
Background

The solution composition and solid phase structures of alkoxy-(alkyl)magnesium compounds appear to be more complex and diverse than those of Grignard reagents. The alkoxy group forms very strong bridge bonds where the oxygen can be either tri- or tetra-valent. Coates and co-workers (1) investigated several alkoxy(alkyl)magnesium systems by a combination of elemental analysis of products, molecular association studies and proton magnetic resonance spectroscopy. They found that bulky alkoxy groups favored the formation of solvated dimers while compounds with less bulky alkoxy groups often formed unsolvated molecules containing four or even seven monomer units. Structures were proposed, in some cases, which accounted for the molecular association results. However, the proton magnetic resonance spectra were often more complex than these structures would suggest and the authors described the spectra as "anomalous in unexplained ways".

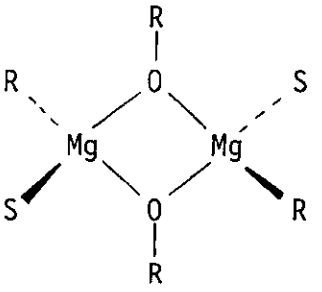
More recently, Nackashi (2) has examined similar systems using these same experimental techniques and low temperature proton magnetic resonance studies. His data were not consistent with simple static structures and complex equilibria involving numerous components were invoked. The structures and equilibria were precedented and reasonable, and the proposed systems were consistent with the experimental

observations provided specific equilibrium and rate constants were imposed.

While the workers cited in the preceding paragraphs have found that alkoxy(alkyl)magnesium reagents can be obtained in several forms with different physical and chemical properties, no basic theories concerning the thermodynamic and kinetic relationships between these structures have been developed. In the current studies, an attempt is made to understand the thermodynamic and kinetic relationships between such structures as those shown below (I - VII) and to develop concepts which systematize the study of these compounds while avoiding ad hoc rationales.



I



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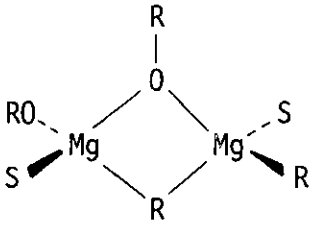

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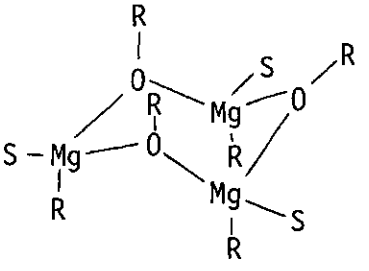

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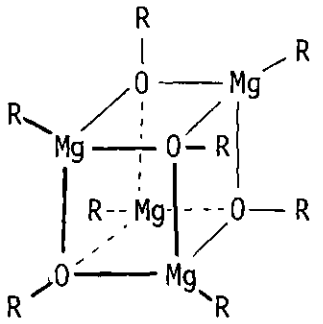

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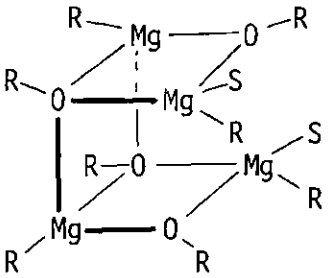
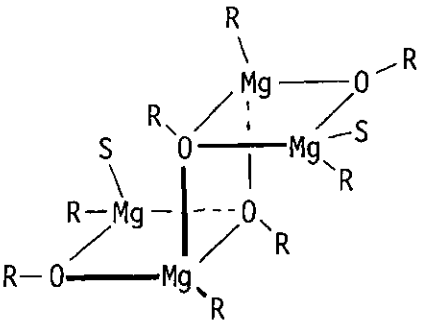
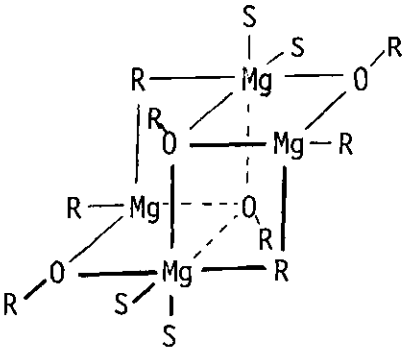


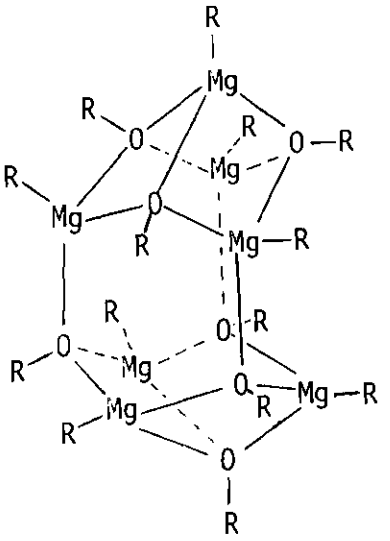
VI-A



VI-B



VI-C



VII

It is probably worthwhile to cite some of the precedents for structures I - VII, particularly the more exotic cage oligomers. Evidence for these structures has come from spectroscopic, molecular association and crystallographic studies. In some cases, precedents are taken from compounds of metals such as aluminum or zinc which have properties similar to magnesium in some aspects.

The evidence for structures of type II comes principally from molecular association studies, but it gains appreciable support by the isolation of crystalline solids with the formula "RMgOR·S" and the observation that magnesium is usually found to be tetracoordinate. The examples cited by Coates (1) are typical.

Structures I and III are offshoots of II which have been invoked in situations where molecular association results indicate dimers in solution but the PMR spectra indicate bridging alkyl groups (2) as

provided by structure III or where the optical rotation of coordinated, optically active ethers indicate that there are three solvent molecules per dimer (3) as provided by structure I.

The cyclic trimer IV does not offend any of the normal concepts of bonding applied to rationalize the structures of organomagnesium compounds, but the only evidence for such structures is molecular association studies of alkylmagnesium alkoxides (4). The six membered Zn_3I_3 ring is found in the solid phase structure of C_2H_5ZnI (5).

The cubane tetramer V has proven to be a very common structure in organometallic chemistry. The best established examples of the M_4O_4 skeleton are found in potassium t-butoxide (6), methylzinc methoxide (7), and $[Mg_4(OCH_3)_2(HOCH_3)_{10}]Cl_2$ (8). While it is seldom stated explicitly, the central M_4O_4 skeleton of these compounds is not a perfect cube.

The "modified cubanes" (VI-A, VI-B, VI-C), as they have been called (2), have relatively little direct support. They have been invoked to provide logical mechanistic pathways for conversion of the solvated dimer to the cubane. A structure similar to VI-C has been reported (9). However, in that structure the two six-coordinate magnesium atoms were coordinated only to electronegative groups (halogens). It is believed that the presence of bridging alkyl groups in VI-C is less likely.

Crystallographic evidence for heptamers of type VII has come recently from the study of aluminum-nitrogen compounds (10,11). However, molecular association and PMR studies suggested that such compounds may be fairly common when the combined steric bulk of the organic groups

bound to oxygen and the metal is small. For example, Coates (1) reports several RMgOR systems which may have structures similar to VII and a novel methylzinc methoxide $(CH_3)_6Zn_7(OCH_3)_8$ has been reported (12).

Purpose

The objectives of this research are to examine alkoxy(alkyl)-magnesium compounds from three standpoints: first, what structures are observed and why are they preferred above other possibilities on the basis of their thermodynamic stability; second, what type of mechanistic pathway leads to the formation of the preferred structures; third, what type of exchange reactions occur among the various environments in which an alkoxy or alkyl group may be found in a given structure.

CHAPTER II

EXPERIMENTAL

Synthesis and Analysis

General Procedures

All methylmagnesium compounds are air sensitive and all reactions were carried out with the aid of a dry box (13) or syringes under nitrogen.

All solvents were distilled from reactive hydrides prior to use (benzene and toluene from NaH, tetrahydrofuran from $NaAlH_4$, and diethyl ether from $LiAlH_4$). All spectroscopic samples were prepared in a nitrogen filled dry box.

Preparation of Dimethylmagnesium

Dimethylmagnesium was prepared by reacting neat dimethylmercury (Orgmet) with a 100% excess of sublimed magnesium metal (Dow) at room temperature for 24 hr (14). After evacuating to remove any unreacted dimethylmercury, the dimethylmagnesium was extracted from the amalgam by adding the solvent of choice (diethyl ether or tetrahydrofuran). Clear colorless solutions were obtained by filtration. Usually the reaction was scaled to obtain about 500 ml of 0.5 M solution. Typically, the ratio of hydrolyzable methyl to magnesium was 1.96:1.00.

Purification of Alcohols

Alcohols (t-butanol, i-propanol and n-propanol) were dried by refluxing over CaH_2 followed by fractional distillation.

Preparation of Alkoxy(methyl)magnesium Compounds

General. In the course of these studies the alkoxy(methyl)-magnesium compounds have been prepared many times. Typical preparations and representative analytical results are described in the paragraphs below. Modifications of the procedures cause no problem as long as the precautions stressed below are followed.

1,1-Diphenylethoxy(methyl)magnesium. Benzophenone (0.025 mole, 4.55 gr in 30 ml of diethyl ether) was added as an ether solution to a stirred solution of dimethylmagnesium (0.025 mole, 45 ml of a 0.56 M solution in diethyl ether) which had been cooled with a dry ice bath. The orange colored reaction mixture was allowed to warm slowly. After two hours the solution had warmed to room temperature and was colorless. When left undisturbed overnight, a deposit of colorless, translucent crystals formed. These crystals were filtered in the dry box and dried under nitrogen (yield 5.1 gr). A weighed sample was analyzed by vacuum line techniques and EDTA titration for CH_4:Mg ratio and %Mg. The results were CH_4:Mg, 1.00:1.00; Mg 7.83%, calculated for "$CH_3MgOC(CH_3)(C_6H_5)_2 \cdot (C_2H_5)_2O$", 7.82% Mg.

A sample of the solid monoetherate lost less than 1% in weight when kept at 25° and 10^{-4} to 10^{-5} mm Hg for one day. When heated at 100° and 10^{-4} to 10^{-5} mm Hg for 18 hr a total of 24% weight was lost (theoretical weight loss for desolvation is 23.8%). Further heating at 100° and then at 125° in vacuo for a total of two days resulted in no significant change in weight. No tendency to sublime or decompose was noted under these conditions.

t-Butoxy(methyl)magnesium, Kinetic Form. Dimethylmagnesium in diethyl ether (typically 0.5 M) was placed in a round bottom flask with a stirring bar and equipped with a three-way stopcock. The solution was cooled in a dry ice/acetone bath to maintain as low a temperature as possible without inducing precipitation. From a syringe, one mole equivalent of a solution of t-butanol in either diethyl ether or benzene (typically 2×10^{-3} mole/gr of solution) was added dropwise to the dimethylmagnesium solution. After addition of all the t-butanol, the reaction mixture was stirred briefly to ensure that evolution of methane was complete. The cold bath was removed and a vacuum was applied to the reaction flask. Evaporation of the solvent kept the reaction mixture cool and virtually all the solvent was evaporated below 0°. The total time from the beginning of the reaction until isolation of the product was less than two hours. Typically, the ratio of hydrolyzable methyl groups to magnesium in solution prior to isolation of the solid was 0.96:1.00. Typical magnesium analysis of the solid was 20.9%; calculated for "$CH_3MgOC(CH_3)_3$", 21.6% Mg. This material was found to be insoluble in benzene. It did not sublime at 160° in vacuo and it decomposed rather than sublimed when heated in vacuo at 200°.

t-Butoxy(methyl)magnesium, Cubane Form. Dimethylmagnesium was reacted with one mole equivalent of t-butanol in diethyl ether or diethyl ether/benzene solvent at low temperatures. The reaction mixture was allowed to warm to room temperature then refluxed for four days. Each day about one fourth of the solvent was distilled out and replaced with pure benzene. Finally the product was isolated by distilling out

all of the solvent at atmospheric pressure. The product was initially a waxy solid but soon crystallized.

This material was soluble in benzene to the extent of 0.26 m and sublimed at as low as 120° in vacuo. However, 140° was found to give a convenient rate of sublimation for synthetic work. The infrared spectra of the sublimed and unsublimed material were virtually identical. While this form of t-butoxy(methyl)magnesium and the kinetic form described above both have bands characteristic of CH_3 and $(CH_3)_3CO$ groups bound to magnesium in their infrared spectra, there are distinct differences in the spectra. Typical magnesium analysis for the sublimed product was 22.1%; calculated for "$CH_3MgOC(CH_3)_3$", 21.6% Mg.

Kinetic "t-Butoxy(methyl)magnesium/Dimethylmagnesium". Following the procedure described for preparation of the kinetic form of t-butoxy-(methyl)magnesium, one mole equivalent of t-butanol was reacted with two mole equivalents of dimethylmagnesium in diethyl ether. The IR spectrum of the unsolvated product was qualitatively very similar to the kinetic form of t-butoxy(methyl)magnesium.

i-Propoxy(methyl)magnesium. Dimethylmagnesium in diethyl ether (typically 0.5 M) was placed in a round bottom flask with a stirring bar and equipped with a three-way stopcock. The solution was cooled in a dry ice/acetone bath. Via syringe, one mole equivalent of i-propanol in diethyl ether (typically 2×10^{-3} mole/gr of solution) was added slowly to the dimethylmagnesium solution. After addition of the i-propanol, the reaction mixture was stirred and allowed to warm to room temperature. In representative preparations, the ratio of hydrolyzable methyl groups

to magnesium in solution was 1.00:1.00. Integration of PMR spectra indicated the ratio of alkoxy groups to methyl groups bound to magnesium was one to one. The solvent was removed in vacuo to obtain the unsolvated solid product. Calculated for "$CH_3MgOCH(CH_3)_2$", 24.7%; a representative sample analyzed 25.0% Mg.

The unsolvated product obtained in this fashion is readily soluble in diethyl ether, tetrahydrofuran or benzene. When heated to 100 to 105° in vacuo, some white material readily sublimed, but the bulk of the material yellowed. The IR spectrum of the sublimed material was virtually identical to the material originally isolated from solution, but the yellowed material had a substantially different IR spectrum. It seems that the product which was obtained by removing solvent sublimes readily without change. However, it simultaneously decomposes to an involatile yellow substance. No changes were observed in the PMR spectra of i-propoxy(methyl)magnesium in diethyl ether, tetrahydrofuran or benzene over a period of weeks.

n-Propoxy(methyl)magnesium. Dimethylmagnesium in diethyl ether (typically 0.5 M) was placed in a round bottom flask with a stirring bar and equipped with a three-way stopcock. The solution was cooled in a dry ice/acetone bath. Via syringe, one mole equivalent of n-propanol in diethyl ether (typically 2×10^{-3} mole/gr of solution) was added to the dimethylmagnesium solution. After addition of the alcohol solution, the reaction mixture was warmed to room temperature. In representative preparations, the ratio of hydrolyzable methyl to magnesium in solution was 1.02:1.00. Integration of PMR spectra indicated the ratio of alkoxy

groups to methyl groups bound to magnesium was one to one. The solvent was removed in vacuo to obtain the unsolvated solid product. Calculated for "$CH_3MgOCH_2CH_2CH_3$", 24.7% Mg; a representative sample analyzed 24.5% Mg.

The unsolvated product obtained in this fashion is readily soluble in diethyl ether, tetrahydrofuran or benzene. When heated to 120 to 130° in vacuo, the solid yellowed slightly and its IR spectrum changed considerably. A very small (unrecoverable) amount of white solid sublimed.

Physical Studies

Infrared Spectra

Infrared spectra were obtained in fluorolube (4000-1350 cm^{-1}) or nujol (1375-250 cm^{-1}) mulls between cesium iodide plates on a Perkin-Elmer 621 spectrometer.

Proton Magnetic Resonance Spectra

Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer with the standard variable temperature unit. Temperature was calibrated with a methanol standard.

Molecular Association Studies

Ebullioscopic molecular association studies were carried out by the technique developed by Walker and Ashby (15). In Appendix 1, data concerning the effect of too little or too much solvent in the apparatus is discussed, since it is believed that this effect invalidates some of the data obtained by Nackashi (2). In these studies, low solubility of the alkoxy(methyl)magnesium reagents limited molecular association

studies to much lower concentration ranges than studied previously with Grignard reagents (15). The inherently small ΔT_{bp}'s and ΔT_{fp}'s which result, lead to experimental uncertainty in the measurements which could not be ignored. The experimental difficulties are discussed in Appendix 2. Cryoscopic molecular association studies were carried out using an apparatus modified for handling air sensitive compounds. In Appendix 3, the actual data collected on systems studied in this part of the thesis are tabulated.

Interconversion Experiments

Pure t-Butoxy(methyl)magnesium Systems. Two grams of the kinetic form of t-butoxy(methyl)magnesium (F_K) were dissolved in 125 ml of diethyl ether. A small sample was placed in an NMR tube and the remainder was split into five equal portions stored in tightly stoppered 50 ml flasks. The samples were stored in a dry box at 20-25°. At intervals, the solvent was evaporated from a flask and IR spectra of the isolated solid were obtained (nujol mulls). At similar intervals, PMR spectra of the initial solution were made. In the PMR spectra, there is a tendency to overestimate the contribution of the cubane form (F_C) because its signals are sharp and standout above the broad signals of the kinetic form. In the IR spectra it is clear that about three weeks are required for half of the kinetic form to convert to thermodynamic form under these mild conditions. Due to the very slow rate of the forward reaction, $F_K \longrightarrow F_C$, it was impractical to allow these solutions to spontaneously go to equilibrium. However, a sample of the pure cubane form (F_C) prepared by the co-distillation procedure and isolated by sublimation was dissolved in diethyl ether and maintained at 20 to

25° for 14 days. The solvent was removed in vacuo and the IR spectrum of the solid (nujol mull) was found to be identical to that of the starting material (F_C). Therefore, at room temperature in diethyl ether the equilibrium between the kinetic form and the thermodynamic form of t-butoxy(methyl)magnesium lies more than 95% in favor of the thermodynamic form.

In a similar experiment, a sample of the cubane form of t-butoxy-(methyl)magnesium (F_C) was dissolved in tetrahydrofuran and stored at room temperature for 14 days. The solvent was removed in vacuo and the IR spectrum of the solid was made (nujol mull). In this spectrum, bands for the kinetic and cubane forms of t-butoxy(methyl)magnesium appeared in about equal intensity. To measure the extent of this reversal of the equilibrium, samples of the kinetic and cubane forms were used to prepare two NMR samples using tetrahydrofuran as the solvent. The samples were kept at 20 to 25° in sealed NMR tubes and spectra were run at convenient intervals. Whereas the PMR spectrum of the kinetic form of t-butoxy(methyl)magnesium in tetrahydrofuran showed no change in several weeks, signals for the kinetic form slowly appeared in the sample of the cubane form. Thus, the cubane form is converted to the kinetic form which is thermodynamically favored in tetrahydrofuran.

Mixed t-Butoxy-/i-Propoxy-(methyl)magnesium Systems. A sample of unsolvated, kinetic t-butoxy(methyl)magnesium was divided into two portions. One portion was placed in an NMR tube and dissolved in diethyl ether. To the other portion a similar amount of unsolvated i-propoxy(methyl)magnesium [which appears to be the cubane form though it was isolated under conditions which yielded the kinetic, linear

polymer form of t-butoxy(methyl)magnesium] was added. This mixture was placed in a second NMR tube and also dissolved in diethyl ether. The room temperature PMR spectra of these samples were obtained approximately 30 minutes after preparation and then at intervals of time for several days.

Kinetic "t-Butoxy(methyl)magnesium/Dimethylmagnesium". A sample of the solid product obtained by reacting one mole equivalent of t-butanol with two mole equivalents of dimethylmagnesium in diethyl ether and removing solvent rapidly in vacuo was redissolved in diethyl ether and observed over a period of time. Its PMR spectrum initially showed only a sharp rapid exchange methyl signal. Over a period of days the signals characteristic of the cubane form of t-butoxy(methyl)magnesium appeared and slowly developed. Ultimately the spectrum was consistent with a mixture of the cubane form of t-butoxy(methyl)magnesium and dimethylmagnesium which do not exchange on the NMR time scale.

CHAPTER III

RESULTS AND DISCUSSION

1,1-Diphenylethoxy(methyl)magnesium

Solutions of 1,1-diphenylethoxy(methyl)magnesium were prepared by reacting one mole equivalent of benzophenone with dimethylmagnesium in diethyl ether at low temperature. The maximum solubility of the product was found to be about 0.3 m, but when prepared at higher concentrations a metastable supersaturated solution can be obtained. Crystals deposited by the supersaturated solution on standing at room temperature proved to be "$(C_6H_5)_2CH_3COMgCH_3 \cdot (C_2H_5)_2O$". Over a period of time, ether is lost from the surface of the crystals at room temperature and atmospheric pressure, and the ether may be readily removed at 100° *in vacuo*. In Figure 1 the IR spectra of 1,1-diphenylethanol, A; 1,1-diphenylethoxy(methyl)magnesium monoetherate, B; and the desolvated material, C, are compared in the 850 to 350 cm^{-1} region. The broad, intense bands in the lower part of this region are due to carbon-magnesium vibrations. The single intense band at 490 cm^{-1} in the spectrum of the monoetherate, B, is assigned to terminal magnesium-methyl stretching. The presence of several broad bands, particularly the main band at 580 cm^{-1} in the spectrum of the desolvated material, C, is indicative of methyl bridge bonds (See Appendix 1 of Part II of this thesis). The degree of molecular association (i-value) for diethyl ether solutions of 1,1-diphenylethoxy(methyl)magnesium examined in these studies (0.288 to 0.045 m)

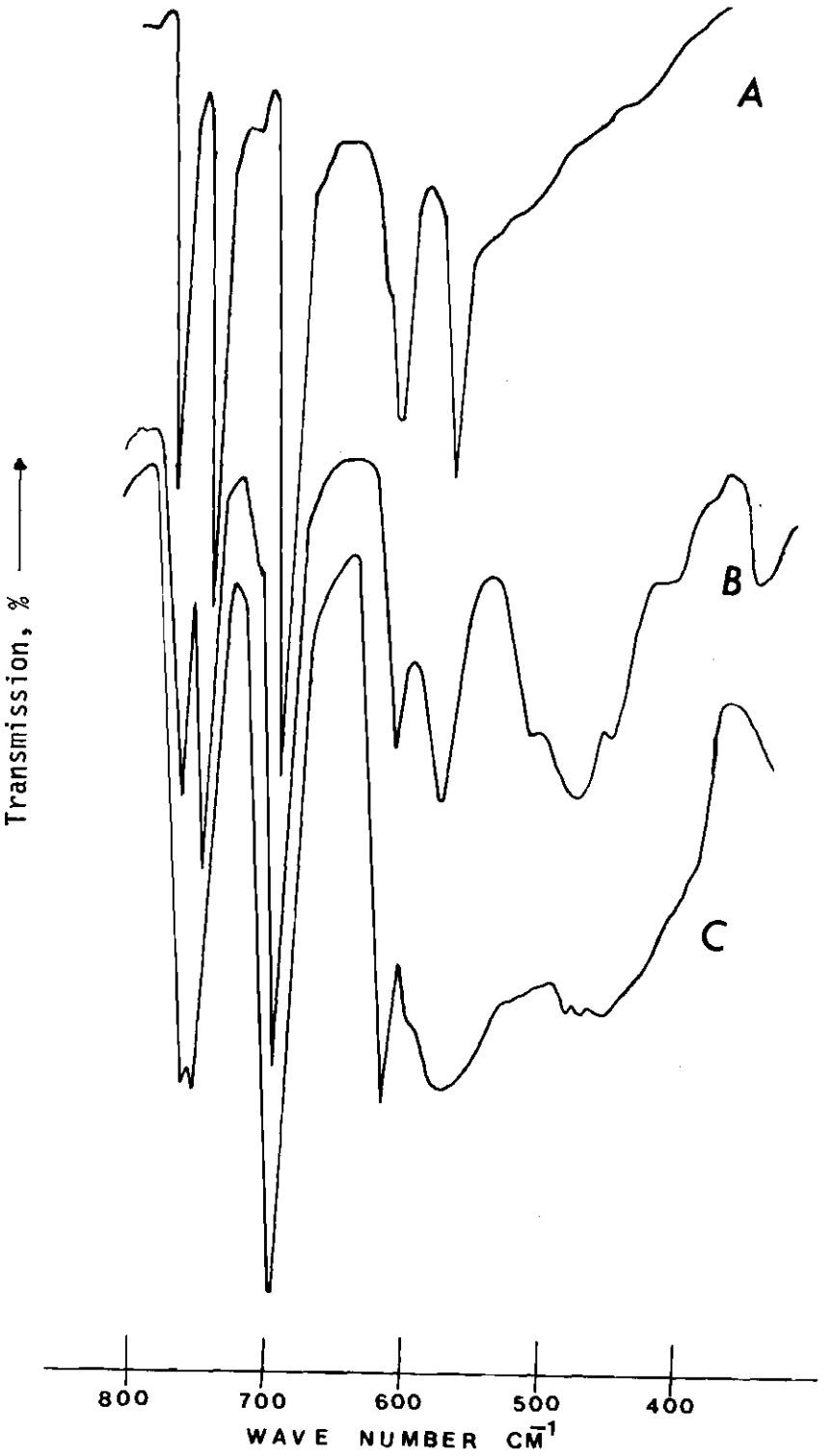
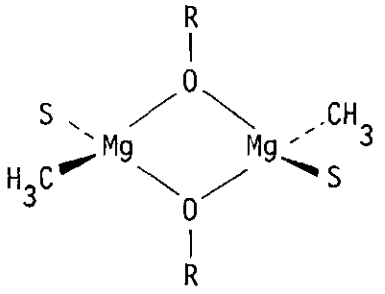


Figure 1. Infrared Spectra of 1,1-Diphenylethanol, A; 1,1-Diphenylethoxy(methyl)magnesium Monoetherate, B; and Desolvated 1,1-Diphenylethoxy(methyl)magnesium, C

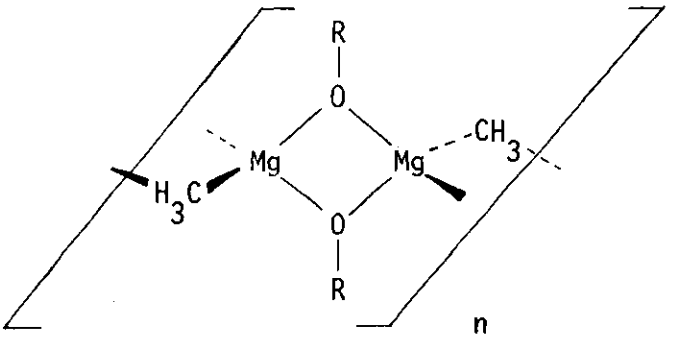
does not vary significantly from 2.0*. The infrared and molecular association data are interpreted as support for the solvated, alkoxy bridged dimer as the primary component in diethyl ether solutions of 1,1-diphenylethoxy(methyl)magnesium (only the trans isomer is shown for brevity).



$S = (C_2H_5)_2O$

$R = (C_6H_5)_2CH_3C-$

Desolvation of this material in the solid phase appears to result in a linear polymer.



During the study of 1,1-diphenylethoxy(methyl)magnesium, there was never any indication that more highly associated components of any

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*Nackashi (2) felt that his data supported a degree of molecular association approaching monomeric (i=1.0) at low concentration. However, it is currently believed that this interpretation does not consider the large (approaching 20%) experimental uncertainty in the ΔT_{bp} measured at low concentration (Appendix 2). In addition, a review of Nackashi's raw data reveal that they were obtained under conditions which would give falsely large ΔT_{bp}'s and small calculated i-values (Appendix 1).

form existed in diethyl ether solution. If there are any more stable forms of this compound, conversion to these forms must be very slow at room temperature in diethyl ether solution, because they were not observed in solutions studied over periods of weeks.

t-Butoxy(methyl)magnesium

In these studies, it has been found that unsolvated t-butoxy-(methyl)magnesium can be isolated in at least two forms. When prepared under conditions favoring isolation of a kinetic product, one form is isolated (F_K) but when thermodynamic equilibrium is achieved in some solvents a different form (F_C) is isolated. The interconversion of these two forms is very slow under most conditions and appears to involve small concentrations of intermediates (F_X) which have not been isolated in pure form. These intermediates often contaminate the principle forms of t-butoxy(methyl)magnesium and are responsible for the "anomalous" PMR spectra reported by Coates and co-workers (1). Without resorting to structural arguments or assignments the interconversions of the various forms of t-butoxy(methyl)magnesium are outlined below.

$$(CH_3)_2Mg + (CH_3)_3COH \xrightarrow{\text{fast}} F_K$$

$$F_K \underset{\text{slow}}{\rightleftharpoons} (F_X) \underset{\text{slow}}{\rightleftharpoons} F_C$$

Preparation under Kinetic Conditions

When one mole equivalent of t-butanol was reacted with dimethylmagnesium in diethyl ether at low temperature and the solvent removed *in vacuo* below 0° as described in the experimental section, unsolvated t-butoxy(methyl)magnesium was isolated in a form (F_K) which is not

soluble in aromatic solvents and does not sublime at temperatures below which decomposition becomes rapid (i.e., 200°). In the infrared spectrum of this form of t-butoxy(methyl)magnesium (Figures 2 and 3), the presence of strong, broad bands at 570, 480 and 390 cm^{-1} is consistent with a methyl bridge bond system with D_2h local symmetry. For a discussion of this assignment see Appendix 1 of Part II of this thesis. The presence of methyl bridge bonds, the involatility and insolubility in aromatic solvents of this form of t-butoxy(methyl)magnesium suggest that it has a linear polymer structure similar to solid dimethylmagnesium.

The kinetic form of t-butoxy(methyl)magnesium dissolves readily in diethyl ether or tetrahydrofuran. Its composition in these solvents was studied by ebulliometry (Appendix 3) and variable temperature proton magnetic resonance spectroscopy. In diethyl ether, the apparent degree of association (i-value) varied from 3.79 ± 0.05 near saturation (0.406 m) to 2.0 ± 0.1 in dilute solution (0.047 m). There was no indication that a preferred degree of association was being approached at high concentration, but extrapolation to infinite dilution suggests that the compound is dimeric at low concentration. This result indicates that in diethyl ether the kinetic form of t-butoxy(methyl)magnesium exists as a complex mixture of polymers which are in rapid, concentration dependent equilibrium. The results of low temperature PMR spectroscopy of a saturated solution is shown in Figure 4. At +40° there is a slightly broadened signal at 11.45τ assigned to terminal methyl sites and a very broad signal centered at 11.20τ assigned to bridging methyl sites. At low temperatures, these two general signals are partially resolved into a number of individual signals. It is impossible

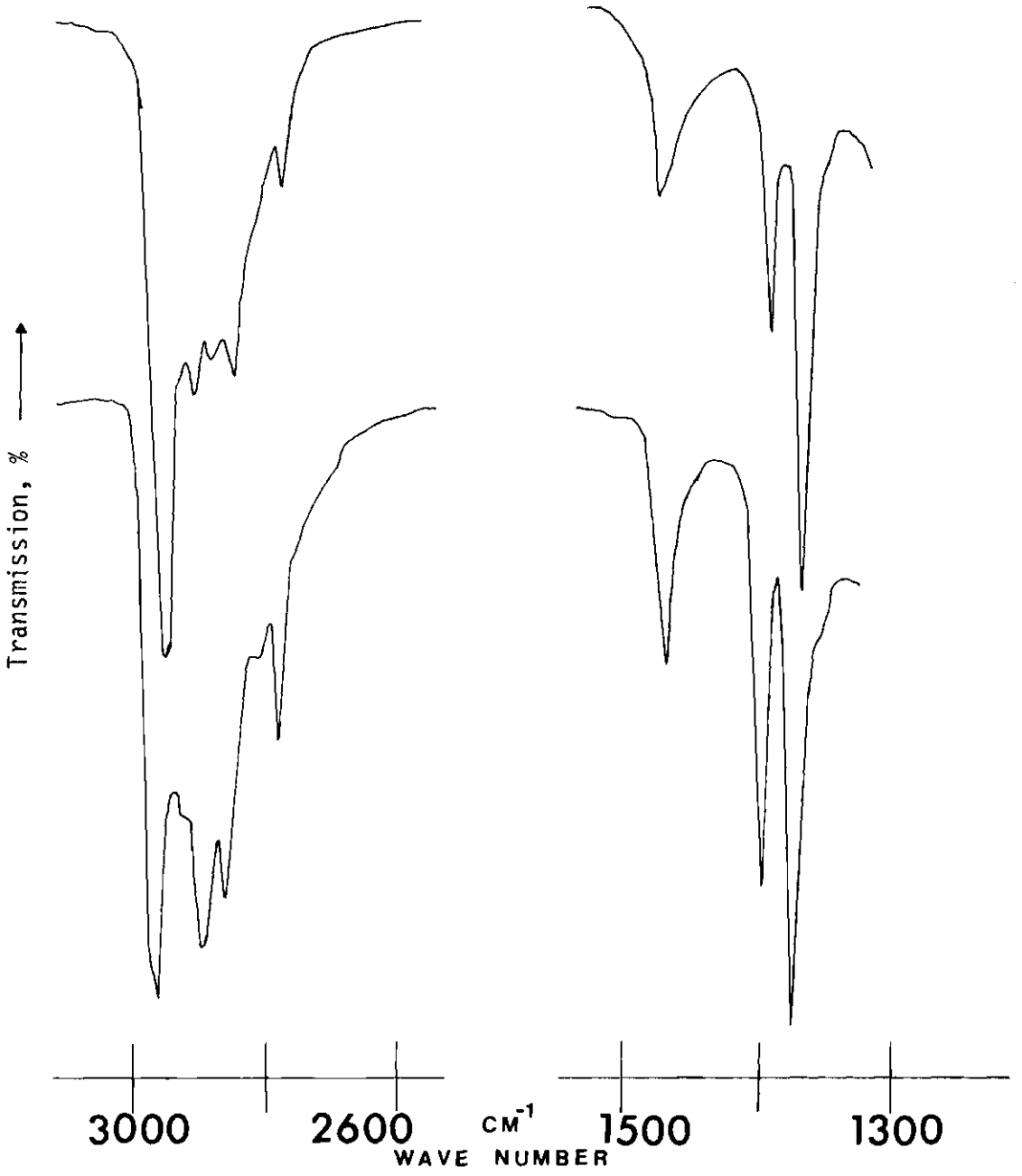


Figure 2. High Frequency Infrared Spectra of Kinetic (Linear Polymer) Form of t-Butoxy(methyl)magnesium, Top; and Cubane Form of t-Butoxy(methyl)magnesium, Bottom

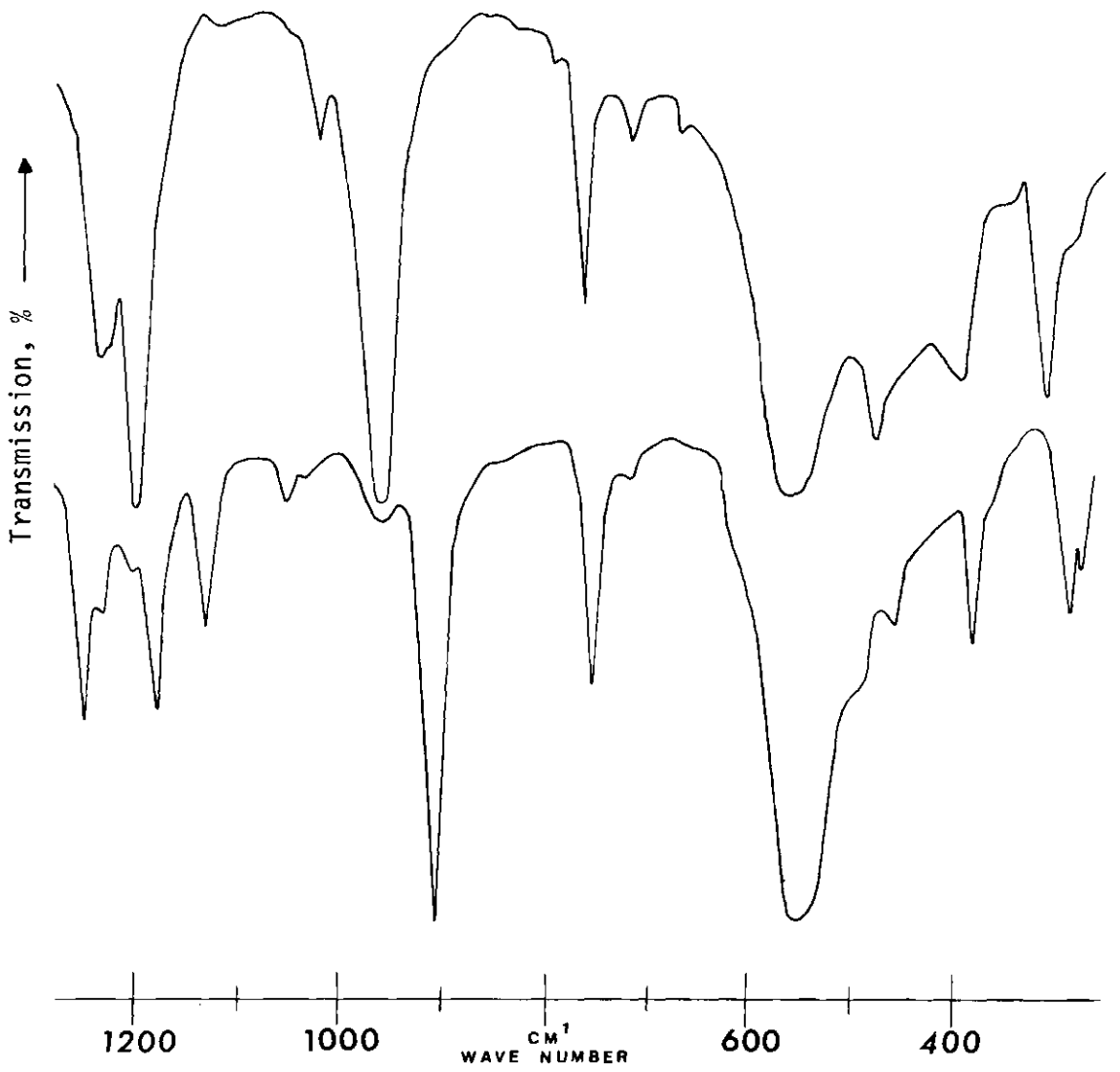


Figure 3. Low Frequency Infrared Spectra of Kinetic (Linear Polymer) Form of t-Butoxy(methyl)magnesium, Top; and Cubane Form of t-Butoxy(methyl)magnesium, Bottom

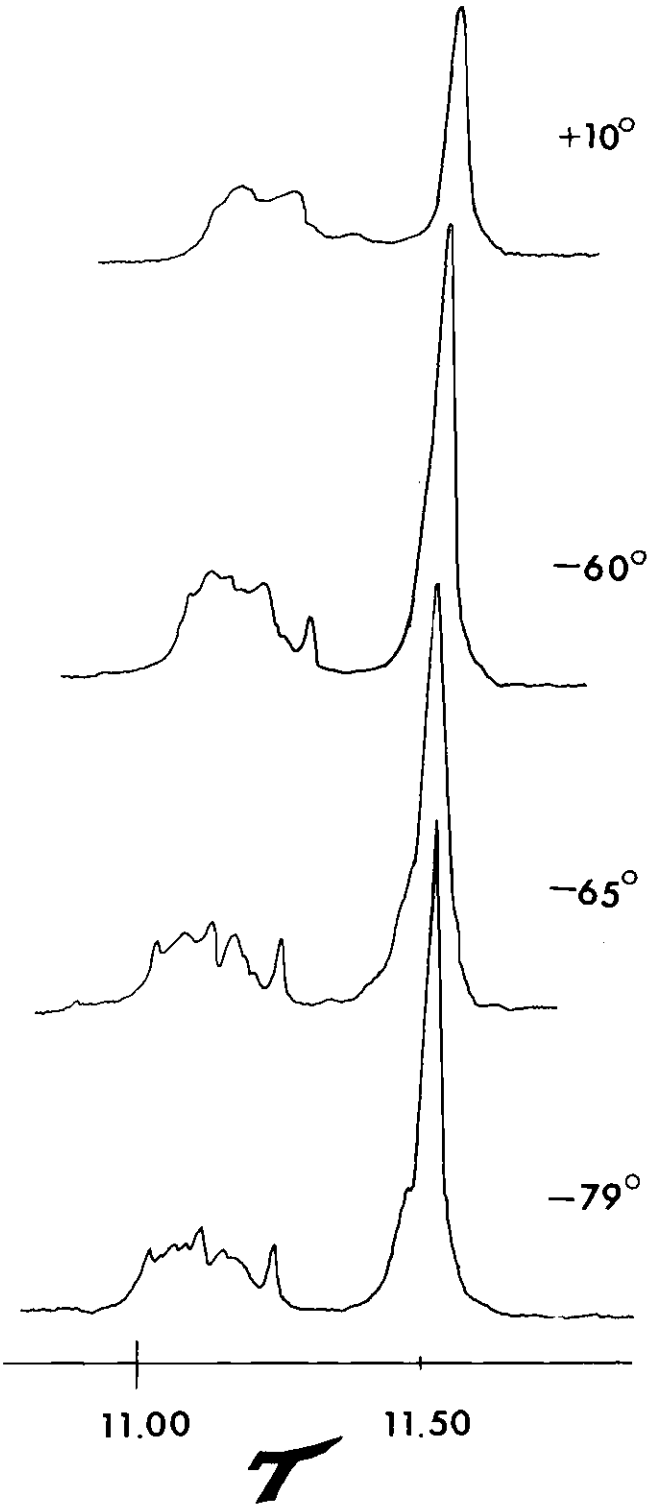
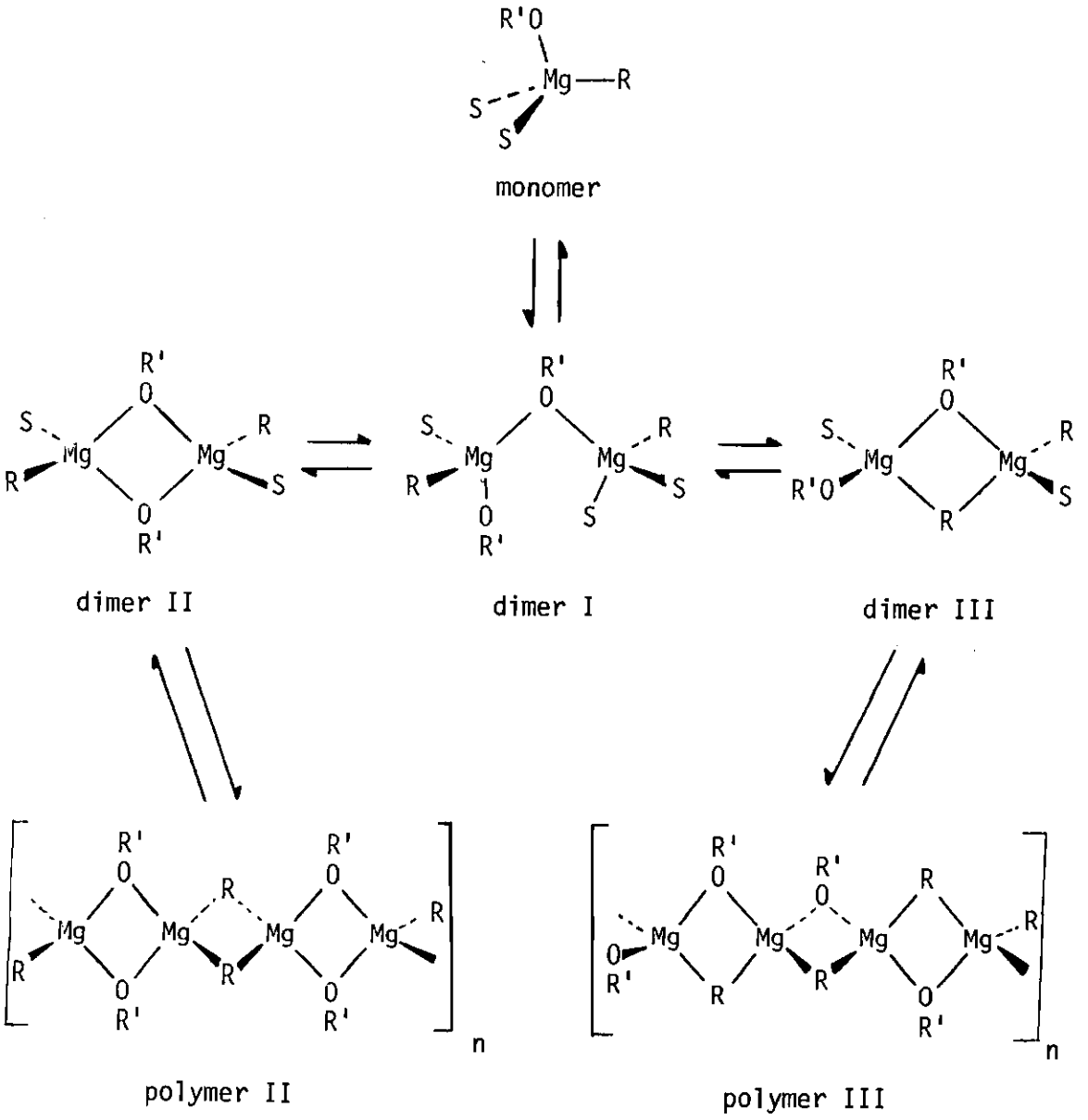


Figure 4. Low Temperature Proton Magnetic Resonance Spectra of the Kinetic Form of t-Butoxy(methyl)magnesium in Diethyl Ether

to assign each methyl signal to a particular chemical structure. However, it is obvious that there are many slightly different methyl sites. It should be noted that these spectra are extremely similar to the spectra of 3-methyl-3-pentaoxy(methyl)magnesium in diethyl ether published by House and co-workers (16). In addition, comparison of these spectra with the spectra of t-butoxy(methyl)magnesium in the presence of an equivalent amount of dimethylmagnesium, as shown in Figure 10, suggests that the sharp signal at 11.33τ and the shoulder at 11.50τ are due to the same chemical species in both systems. The t-butoxy signal falls under the diethyl ether triplet and was not observed.

Thus, the composition of the kinetic form of t-butoxy(methyl)-magnesium in diethyl ether is best represented by a set of complex equilibria. At low concentration, dimers I, II and III predominate while at high concentration there are appreciable amounts of linear polymers like polymer II and polymer III. The involatile solid obtained by removing solvent <u>in vacuo</u> is probably a mixture of polymer II and polymer III.

In tetrahydrofuran, the apparent degree of association (i-value) of the kinetic form of t-butoxy(methyl)magnesium indicates dimeric association even at relatively high concentrations (e.g., greater than 0.4 m). The degree of association does not appear to be greatly affected by concentration. The variable temperature PMR spectra in Figure 5 are consistent with dimer II being the chief component in these solutions. The major t-butoxy signal, 8.80τ, and major methyl signal, 11.60τ, are assigned to II. There are several possibilities for assignment of the minor t-butoxy and methyl signals.



R = CH_3

R' = $(CH_3)C$

S = Solvent

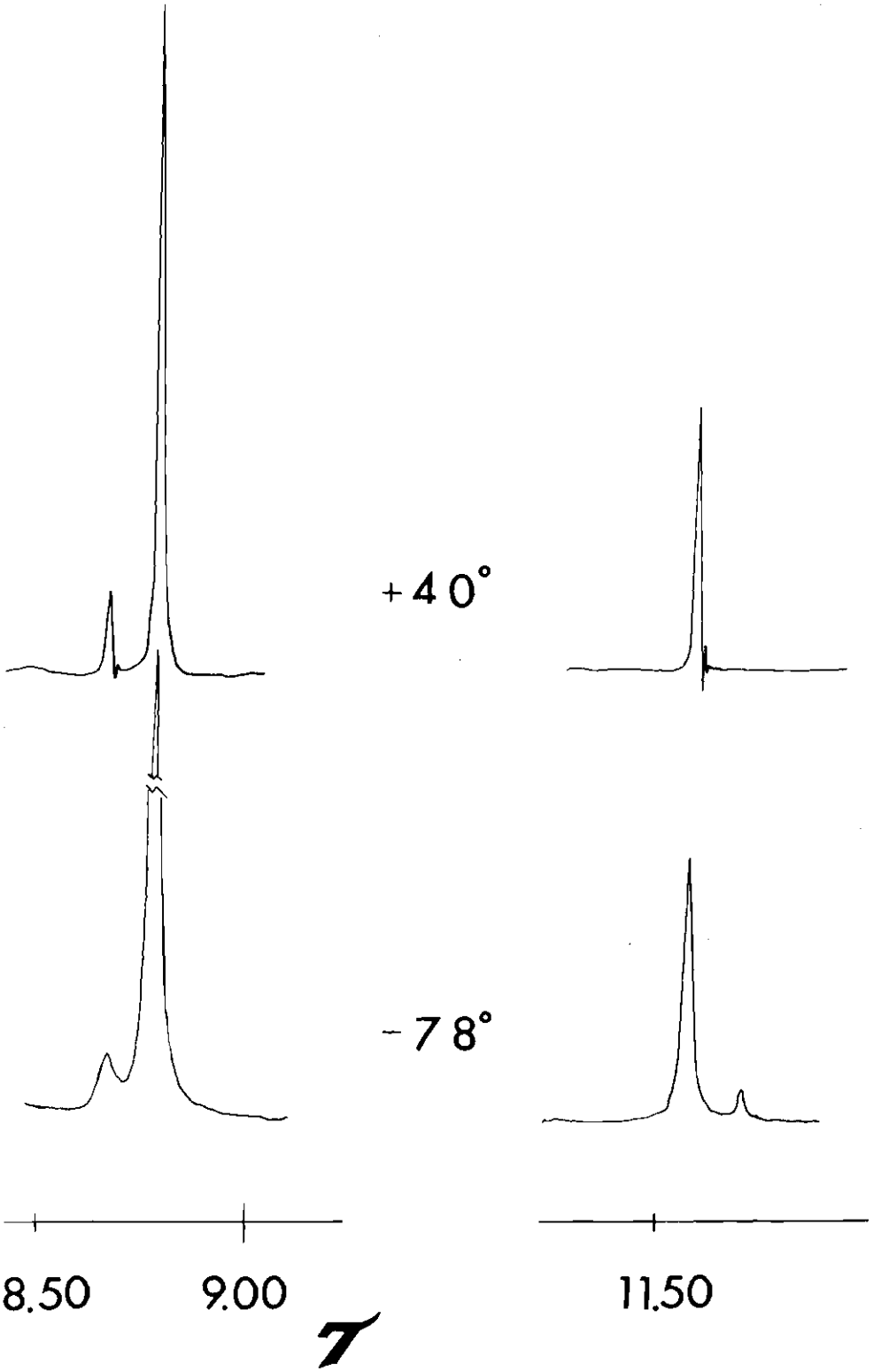
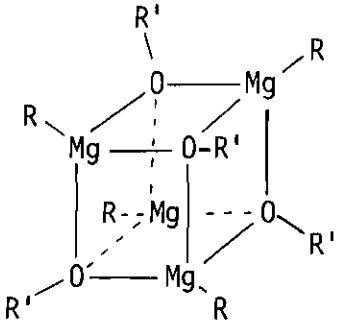


Figure 5. Low Temperature Proton Magnetic Resonance Spectra of the Kinetic Form of t-Butoxy(methyl)magnesium in Tetrahydrofuran

The Cubane Form

Coates and co-workers (1) have reported obtaining t-butoxy-(methyl)magnesium in a cubane form, V. However, their PMR spectra



V

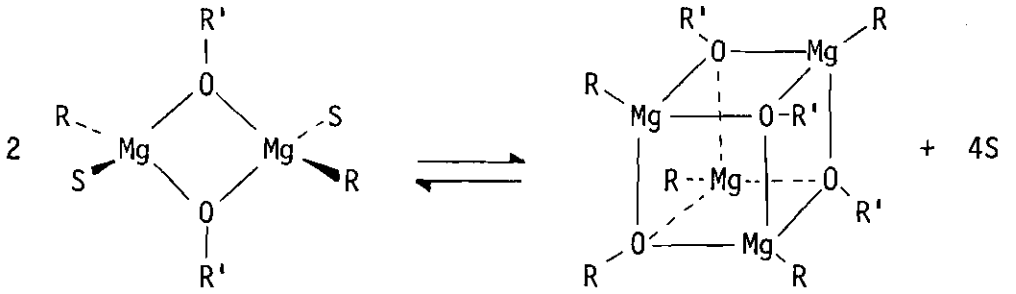
$R = CH_3$, $R' = (CH_3)_3C$

contained unexpected signals. In these studies, it has been found that the cubane form (F_C) of t-butoxy(methyl)magnesium can be prepared without significant impurities by refluxing the diethyl ether solution of the kinetic form (F_K) with benzene co-solvent as described in the experimental section. The cubane form of t-butoxy(methyl)magnesium, prepared by this technique, is soluble in aromatic solvents and readily sublimes without change at 140° in vacuo. The apparent degree of association (i-value) of the cubane form was found to be 4.0 ± 0.2 at 0.202 m, 4.1 ± 0.3 at 0.159 m and 4.4 ± 0.4 at 0.148 m by cryoscopy in benzene. The PMR spectrum of the pure cubane form of t-butoxy(methyl)magnesium contains no unexpected signals. In diethyl ether the t-butoxy signal is at 8.45τ and the methyl signal is at 11.11τ. The alkoxy and alkyl groups are inert to exchange with dimethylmagnesium in diethyl ether on the NMR

time scale. There is no noticeable temperature dependence of the PMR spectrum up to +100° in toluene or down to -100° in diethyl ether. The infrared spectrum of the cubane form of t-butoxy(methyl)magnesium is compared to the kinetic form in Figures 2 and 3. There are a number of obvious differences in the methyl and t-butoxy fundamental bands. As expected, there is also a simplification of the bands in the 600 to 300 cm^{-1} region assignable to the methyl-magnesium vibrations. In contrast to the kinetic form, there is only one major band at 550 cm^{-1} due to the terminal methyl-magnesium stretch.

Interconversion of the Kinetic and Cubane Forms

The equilibrium between the kinetic form and cubane form of t-butoxy(methyl)magnesium is solvent dependent. In diethyl ether or diethyl ether/benzene (relatively nonpolar solvents), the unsolvated cubane form is thermodynamically preferred. However, in tetrahydrofuran (a relatively polar solvent) the solvated kinetic form is thermodynamically preferred. This result is similar to the solvent effects observed in the Schlenk equilibrium of Grignard reagents.



Even though the forward reaction above results in greater association of the organometallic reagent, the entropy for the forward reaction is very likely to be large and positive due to loss of solvation. The enthalpy

for the reaction depends upon the heat of solvation and in diethyl ether the enthalpy for the forward reaction is probably small, and not great enough to override the effect of entropy. On the other hand, in tetrahydrofuran the enthalpy of the forward reaction is unfavorable and large enough to drive the equilibrium to the left. The formation of linear polymers in concentrated diethyl ether solutions of the kinetic form of t-butoxy(methyl)magnesium also appears to be a manifestation of the low heat of solvation by diethyl ether.

In a qualitative kinetic experiment, the $F_K \longrightarrow F_C$ conversion in diethyl ether was followed by a combination of PMR and IR techniques. The time dependence of the room temperature PMR spectra and solid phase IR spectra is demonstrated in Figures 6 and 7 respectively. In each set of spectra one spectrum is marked with the symbols K, C and X to denote absorptions due to the kinetic form, cubane form and intermediate forms respectively. The absorptions marked X do not appear in the spectra of the pure kinetic form or pure cubane form. The PMR spectra of Figure 6 were obtained at the following intervals: A, 0 hr; B, 50 hr; C, 75 hr; D, 266 hr; E, 386 hr. The IR spectra of Figure 7 were obtained at the following intervals: A, 0 hr; B, 50 hr; C, 264 hr; D, 428 hr; E, 723 hr. Notice that because the PMR signals of the cubane form are so sharp and distinct that there is a tendency to overestimate its contribution in the PMR spectra. At room temperature in diethyl ether, about 30 days (720 hr) are required for the reaction to go halfway to completion. It was verified that the equilibrium lies far in favor of the cubane form by dissolving the cubane form in diethyl ether and observing that there was no detectable change in its PMR or IR spectra over a period of

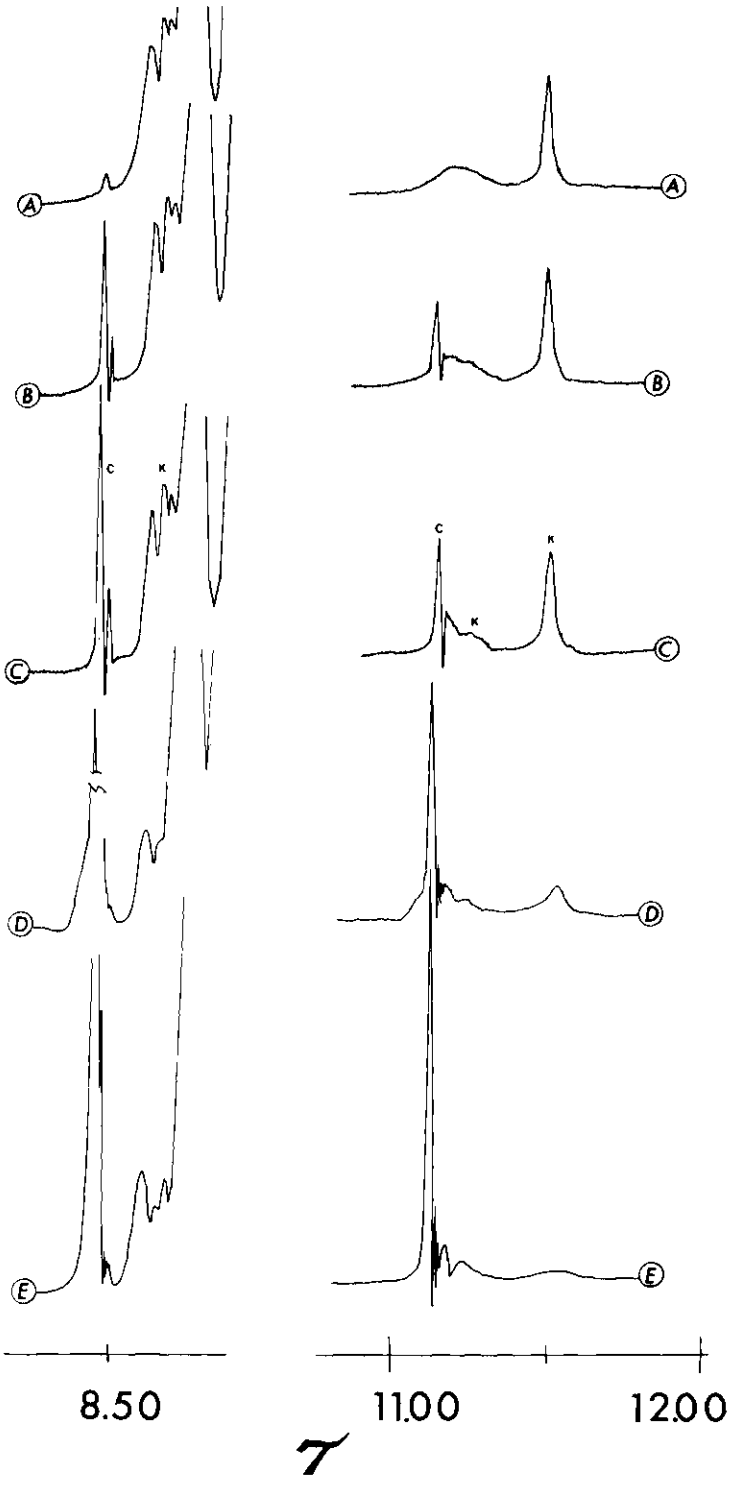


Figure 6. Time Dependence of the Ambient Temperature PMR Spectra of t-Butoxy(methyl)magnesium in Diethyl Ether, Showing Signals for Kinetic Form (K) and Cubane Form (C): Spectrum A at 0 hr; Spectrum E at 386 hr

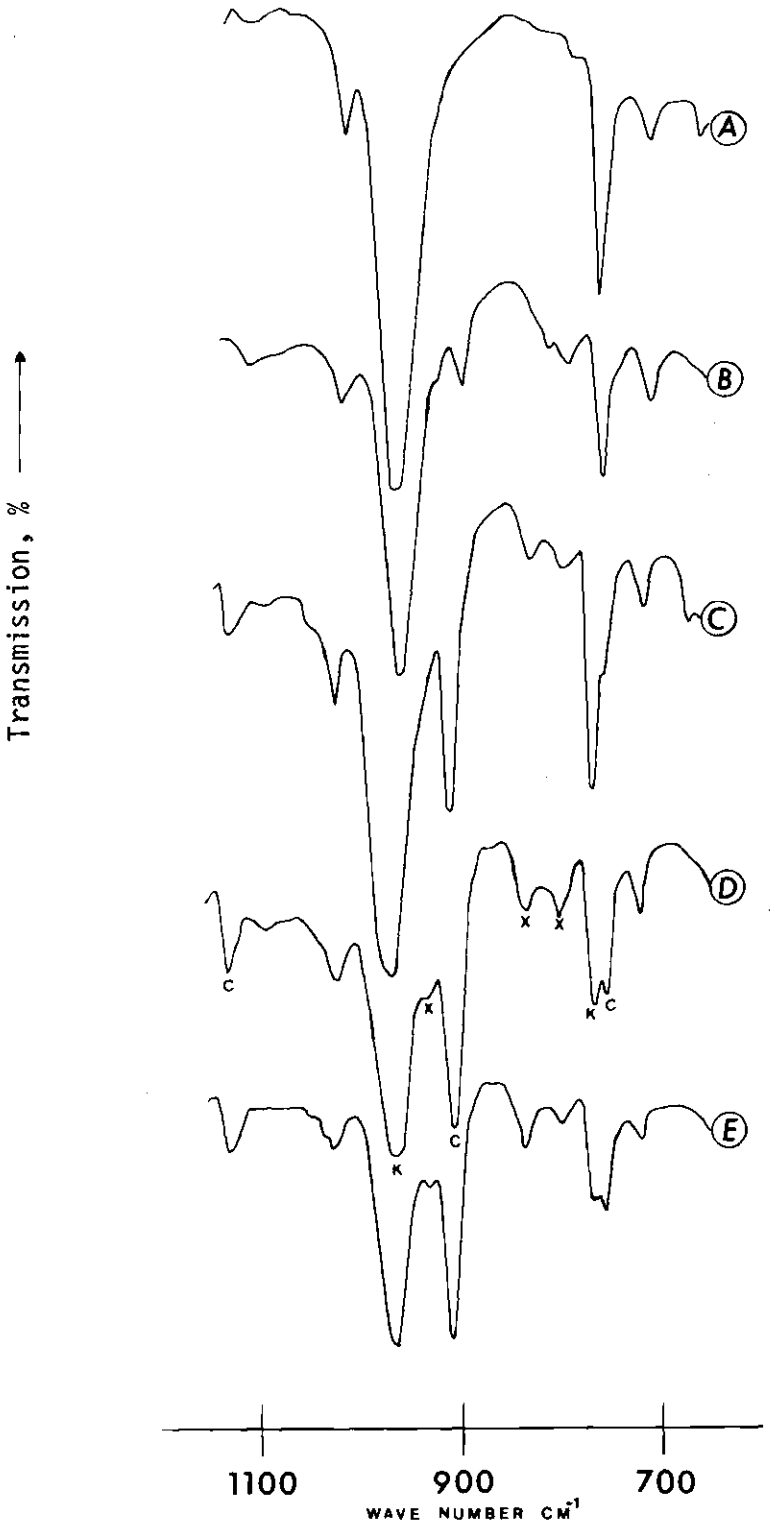


Figure 7. Time Dependence of the IR Spectra of t-Butoxy(methyl)-magnesium, $F_K \longrightarrow F_C$: Spectrum A at 0 hr, Spectrum E at 723 hr

several weeks. When a partially aged sample of solid t-butoxy(methyl)-magnesium is heated in vacuo at 200°, a mixture of the cubane form and some of the volatile intermediates sublime. This procedure is essentially the same that Coates and co-workers (1) used to first isolate the cubane form. Figure 8 shows expanded spectra (sweep width = 100 Hz) of the t-butoxy and methyl region of the PMR spectrum of a sublimed sample of cubane t-butoxy(methyl)magnesium containing signals due to volatile intermediates marked X. In addition, at 9.65τ there is a small sharp signal which may also be due to intermediate forms since it often appears when the other signals are observed and it does not seem to be due to solvent side bands or impurities such as stopcock grease. At this point, it is not clear how many intermediates there are or what type structures they have.

In a similar experiment, a sample of the cubane form of t-butoxy-(methyl)magnesium was dissolved in tetrahydrofuran. The sample was stored at room temperature and the PMR spectrum was obtained at intervals as shown in Figure 9: A, 0 hr; B, 142 hr; C, 396 hr. Here again, the equilibrium between the principal forms is established very slowly. The equilibrium was found to lie far in favor of the solvated dimer of the kinetic form by dissolving a sample of the kinetic form in tetrahydrofuran and observing that there was no indication of the signals for the cubane form after several weeks.

Interaction of Kinetic t-Butoxy(methyl)magnesium with Excess Dimethylmagnesium

Because of the very slow interconversion of the linear polymer and cubane forms of t-butoxy(methyl)magnesium it is possible to examine

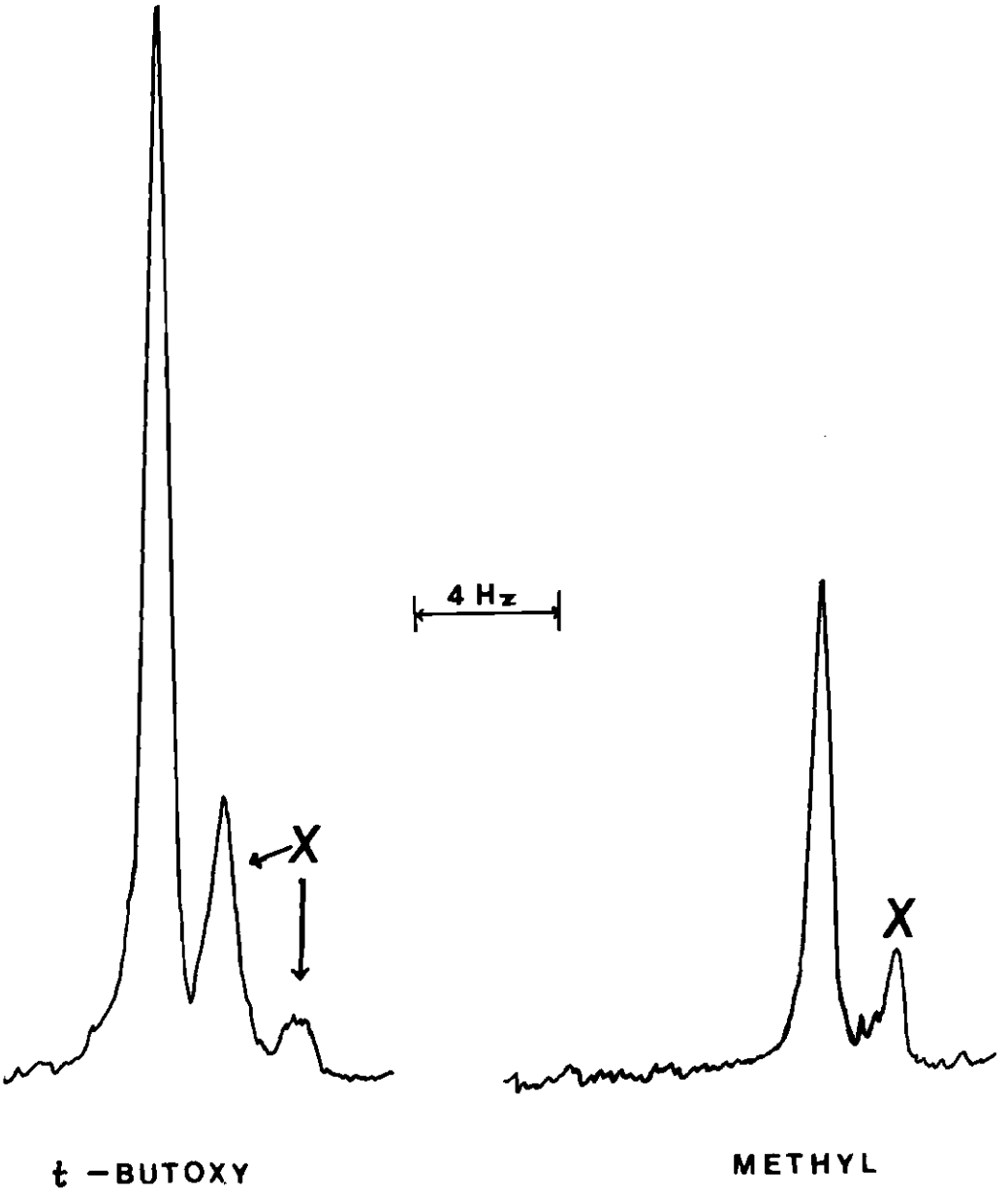


Figure 8. PMR Spectrum of t-Butoxy(methyl)magnesium in Diethyl Ether at Ambient Temperature Showing Signals for Intermediates (X)

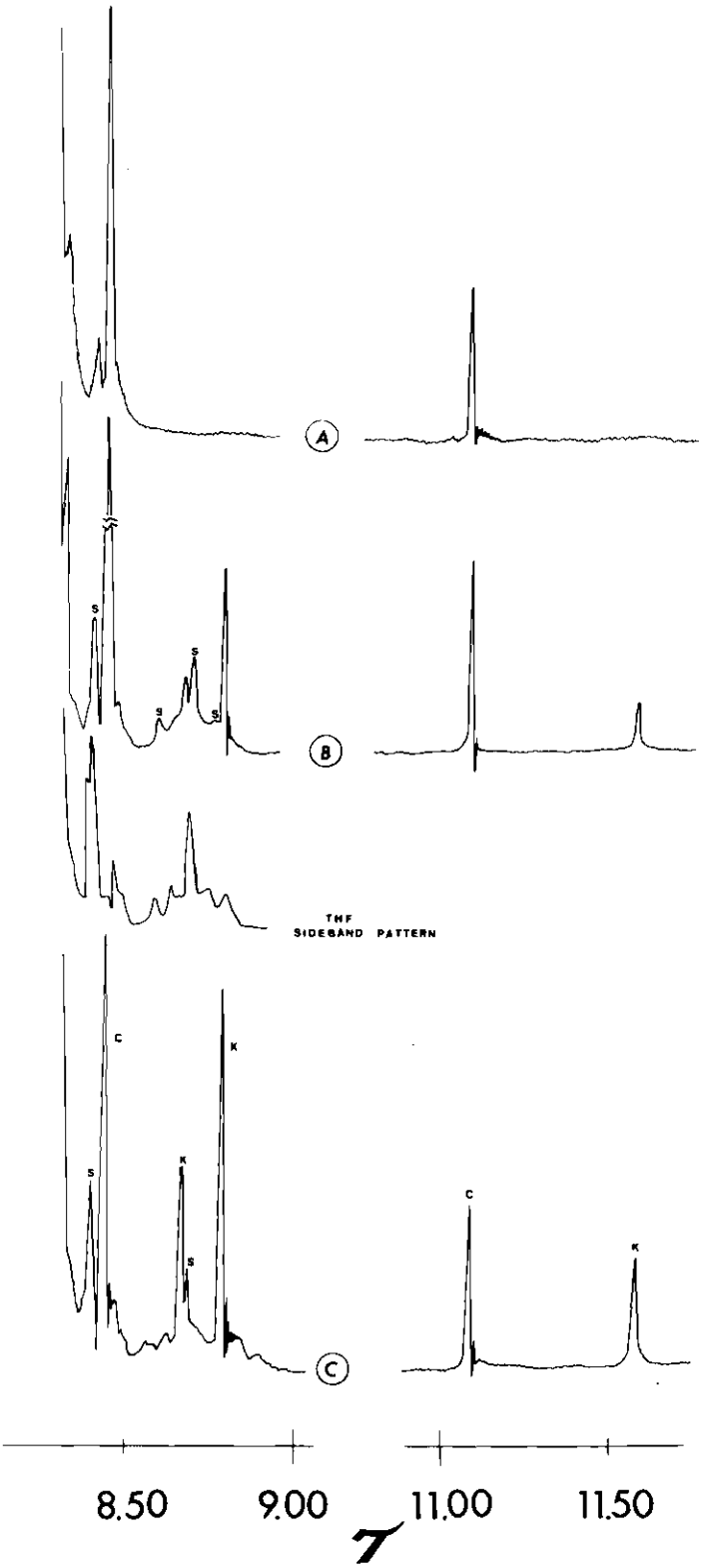
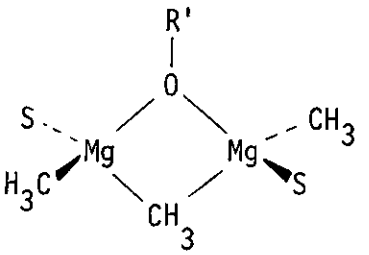


Figure 9. Time Dependence of Ambient Temperature PMR Spectra of Cubane t-Butoxy(methyl)magnesium in Tetrahydrofuran, $F_C \longrightarrow F_K$

the interactions of these two forms with dimethylmagnesium in diethyl ether independently. As noted above, the cubane is very inert and does not exchange alkyl groups with or otherwise detectably interact with dimethylmagnesium. On the other hand, the kinetic form readily exchanges methyl groups with dimethylmagnesium and apparently forms complexes containing mixed alkoxy-alkyl bridges. The variable temperature PMR spectrum of a solution prepared by reacting one mole equivalent of t-butanol with two mole equivalents of dimethylmagnesium is shown in Figure 10. At room temperature the methyls bound to magnesium give only a time averaged signal. At -54° two signals are resolved. The signal at 11.33τ is assignable to bridging methyls and a signal at 11.45τ appears to be an exchange averaged signal for terminal methyls since lowering the temperature to -80° results in broadening of the high field signal. Unfortunately, the high field signal could not be resolved into other signals above -100° where resolution of the spectrum markedly deteriorated. The IR spectrum of the material obtained by removing solvent from this reagent soon after preparation was qualitatively very similar to that of the kinetic form of t-butoxy(methyl)-magnesium. As suggested by Nackashi and Ashby (17), the bridging methyl signal can be explained best by a mixed bridge structure.



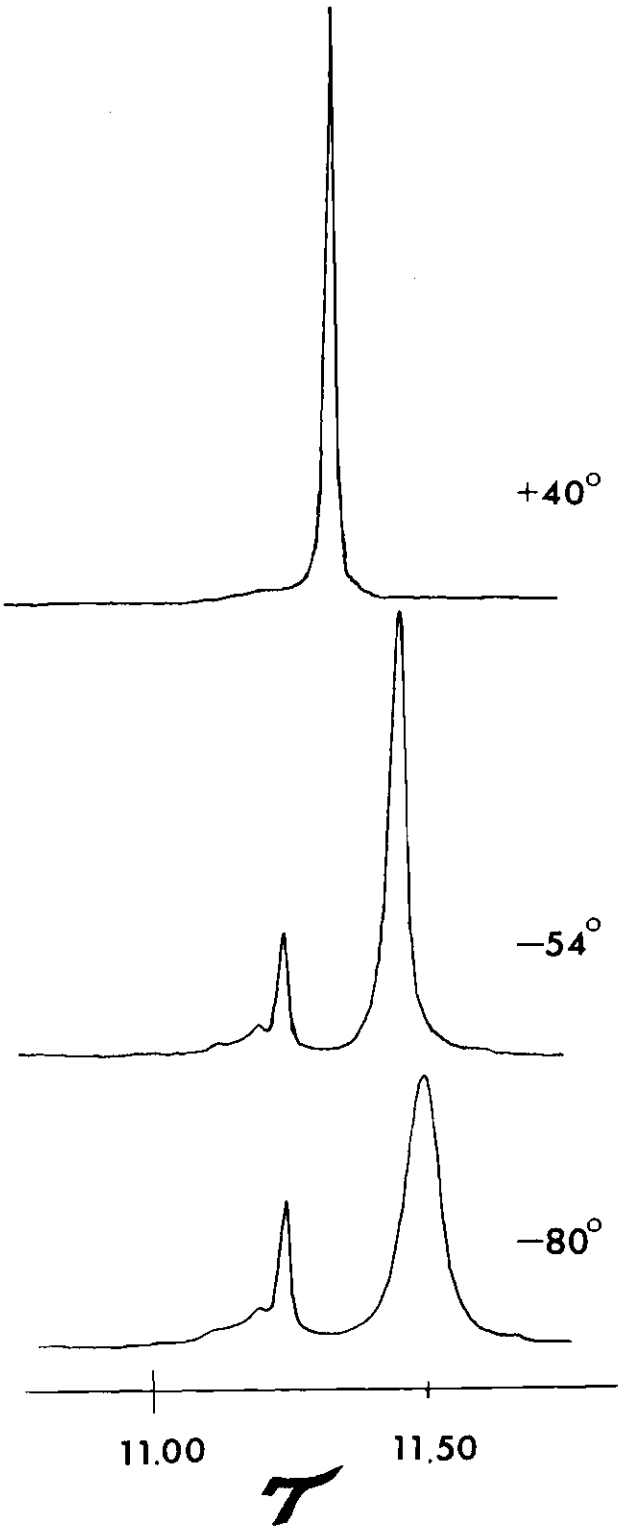
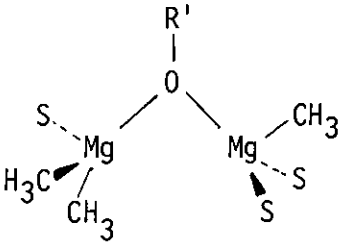


Figure 10. Low Temperature PMR Spectra of Kinetic t-Butoxy(methyl)magnesium Plus One Mole of Dimethylmagnesium in Diethyl Ether

However, the terminal to bridging methyl ratio is observed to be much greater than 2:1 so other species must be involved. On the basis of molecular association studies of the system $(C_6H_5)_2CCH_3OMgCH_3/(CH_3)_2Mg$, Nackashi and Ashby suggested that a half bridged structure could account for the excess of terminal methyls in the system.



Such species have recently been shown to be important components in organomagnesium systems. However, even with molecular association results, it is difficult to rule out some contribution from a disproportionation equilibrium involving uncomplexed dimethylmagnesium and the alkoxy bridged dimer. Furthermore, it is significant that when this reagent is allowed to age, it slowly converts to a mixture of the cubane form of t-butoxy(methyl)magnesium and dimethylmagnesium. While mixed bridge species undoubtedly exist in these systems, dimethylmagnesium does not appear to complex the alkoxy(methyl)magnesium compounds strongly enough to prevent conversion to the cubane.

i-Propoxy(methyl)magnesium

Reinterpretation of Nackashi's observations of i-propoxy(methyl)-magnesium (2) employing the concepts developed in the current study of t-butoxy(methyl)magnesium and interpretation of additional experimental results reported for the first time here suggest that the same

structures found in the t-butoxy(methyl)magnesium system (i.e., dimers, linear polymers and cubane) are involved in the i-propoxy(methyl)magnesium system. The thermodynamic stabilities of the components in the various solvents are similar to the t-butoxy(methyl)magnesium system, but the equilibrium between the dimer and linear polymer forms and the cubane form is established very rapidly.

When one mole equivalent of i-propanol was reacted with dimethylmagnesium in diethyl ether at low temperature and the solvent was removed below room temperature in vacuo, unsolvated i-propoxy(methyl)-magnesium was isolated in a form which is soluble in diethyl ether, tetrahydrofuran or benzene. The solid sublimed at 100 to 105° in vacuo, but simultaneously decomposed to an involatile, pale yellow solid even under these mild conditions. The IR spectrum of the solid obtained from solution is the top spectrum in Figure 11. The absence of a strong absorption at 600-575 cm^{-1} suggests the absence of a methyl bridge system. See Appendix 1 of Part II of this thesis. The IR spectrum of the yellow decomposition product is the bottom spectrum in Figure 11.

The PMR chemical shifts of the signals for the methyl groups of the i-propoxy groups and methyl groups bound to magnesium are similar to the shifts of the methyl groups of the t-butoxy group and methyl group bound to magnesium of the cubane form of t-butoxy(methyl)magnesium in diethyl ether or benzene. See Table 1. This result is consistent with i-propoxy(methyl)magnesium having a cubane structure in these solvents. Alternately, there could be a rapid equilibrium in which the cubane is a major constituent. These arguments are supported by molecular association results since the unsolvated compound dissolves readily in benzene

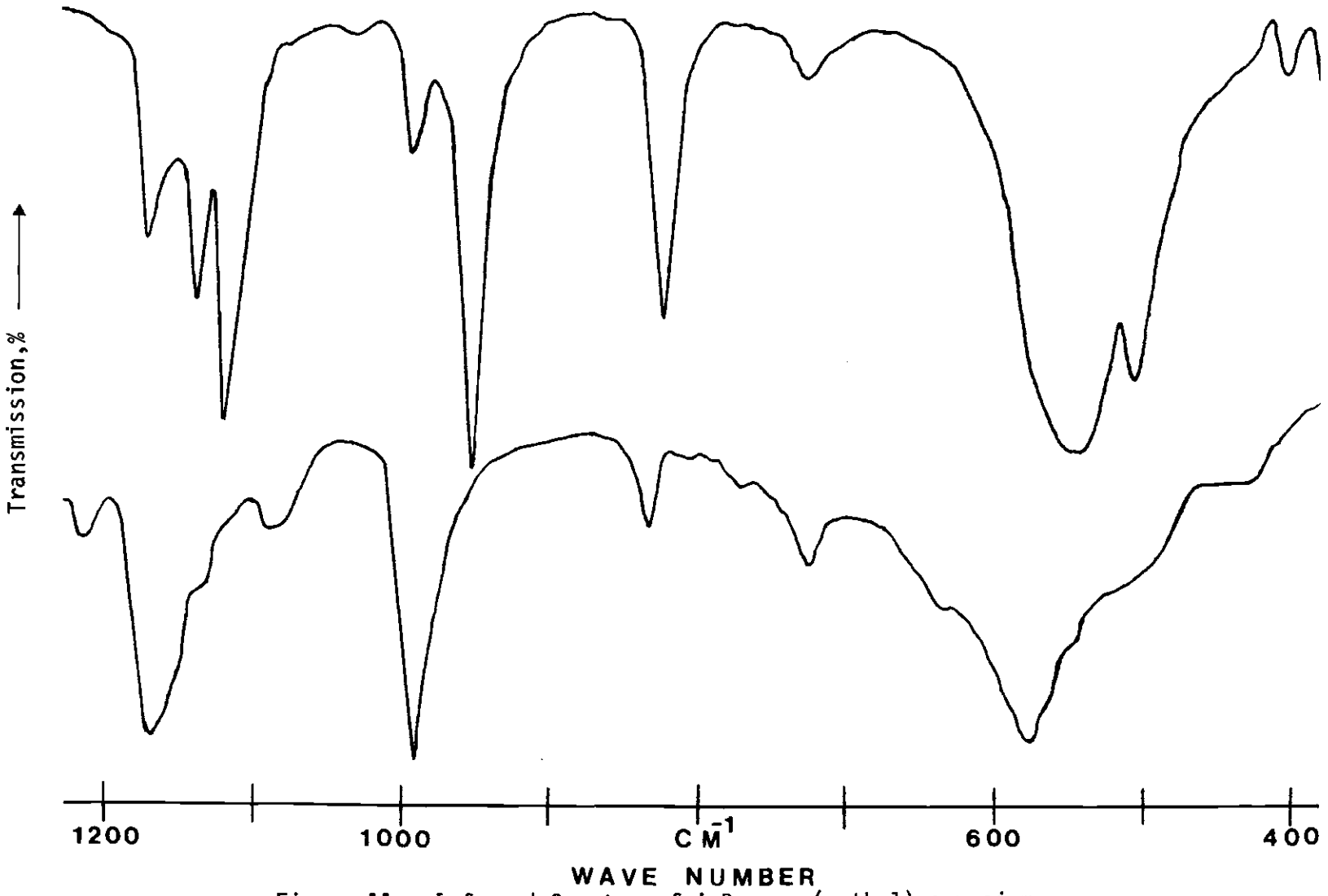


Figure 11. Infrared Spectra of i-Propoxy(methyl)magnesium, Top; and Its Decomposition Product when Heated to 105°, Bottom

Table 1. PMR Chemical Shifts for Various Forms of the Alkoxy(alkyl)magnesium Compounds in Several Solvents

Compound	Form	Solvent	Chemical Shift (τ)	
			OCR_2-CH_3	Mg-CH_3
CH_3MgOBu^t	cubane	benzene	8.53	10.66
		diethyl ether	8.45	11.11
		tetrahydrofuran	8.45	11.12
CH_3MgOBu^t	linear polymer	diethyl ether	~8.8	11.20,11.45
CH_3MgOBu^t	dimer	tetrahydrofuran	8.80	11.60
CH_3MgOPr^i	(cubane)	benzene	8.70	10.76
	(cubane,linear polymer)	diethyl ether	8.52	11.30
	(dimer)	tetrahydrofuran	8.88	11.66
CH_3MgOPr^n	(unsolvated oligomer)	benzene	--	10.82
	(cubane,linear polymer)	diethyl ether	--	11.33
	(dimer)	tetrahydrofuran	--	11.70

where cryoscopic measurements indicate that it is tetrameric, i = 4.08 ± 0.07 at 0.474 m, i = 4.21 ± 0.10 at 0.353 m and i = 4.29 ± 0.14 at 0.277 m. In diethyl ether the apparent degree of association is consistent with a rapid equilibrium between tetramers, dimers and linear polymers since the i-values vary significantly with concentration, i = 3.67 ± 0.07 at 0.492 m to i = 2.83 ± 0.14 at 0.140 m (see Appendix 3 for complete data). The low temperature PMR spectra of i-propoxy(methyl) magnesium in diethyl ether reported by Nackashi (2) and verified during these studies show that the 11.30τ signal observed at room temperature, assigned here to an exchange averaged signal representing a large contribution from cubane sites, is predominant at low temperature though a second signal 11.60τ is resolved at -60° and grows to equal intensity at -80°. It should be noted that at low temperature almost all the i-propoxy(methyl)magnesium precipitates so that the ratios of the components in solution could be the result of selective precipitation. In the original interpretation of these spectra (2), it was assumed that all methyl groups bound to magnesium by two-center two-electron bonds (i.e., terminal methyl groups) should give PMR resonance at greater than about 11.50τ regardless of the overall structure in diethyl ether solution. It naturally followed that in these spectra the low field signal was assigned to bridging sites and the high field signal was assigned to terminal sites. In the t-butoxy(methyl)magnesium system it was found that the terminal methyl groups of the cubane tetramer absorb at low field (11.1-11.2τ) in diethyl ether. This region of the spectrum was previously reserved for methyl groups involved in multicenter electron deficient bonding (18).

When the i-propoxy(methyl)magnesium obtained as described above is dissolved in tetrahydrofuran, its PMR chemical shifts for the methyls of the i-propoxy group and methyl bound directly to magnesium are similar to those of the t-butoxy group and methyl group of the dimeric form(s) of t-butoxy(methyl)magnesium in the same solvent. See Table 1. The molecular association data for i-propoxy(methyl)magnesium in tetrahydrofuran also indicate a dimeric composition i = 1.78 ± 0.06 at 0.124 m, i = 2.07 ± 0.06 at 0.153 m and i = 2.00 ± 0.05 at 0.189 m.

Thus, the molecular association and PMR results for i-propoxy-(methyl)magnesium indicate that in solution it prefers the same structures as t-butoxy(methyl)magnesium in the respective solvents. However, the equilibrium composition is achieved very rapidly and no time dependent phenomena such as observed in the t-butoxy(methyl)magnesium system were observed.

If the conclusions that the i-propoxy(methyl)magnesium system in diethyl ether contains labile cubane tetramers while t-butoxy(methyl)-magnesium cubane tetramers are very inert to exchange reactions in the same solvent is correct, it should be possible to obtain an equilibrium mixture of mixed alkoxy cubane tetramers in which some of the mixed cubanes are labile and some fairly inert depending upon the number of t-butoxy and i-propoxy groups which they incorporate. This hypothesis was tested by adding some i-propoxy(methyl)magnesium to a sample of the kinetic form of t-butoxy(methyl)magnesium in diethyl ether. The room temperature PMR spectrum of the mixed system was compared to the spectrum of a sample of the kinetic t-butoxy(methyl)magnesium which was prepared simultaneously (Figure 12). Whereas the pure t-butoxy system

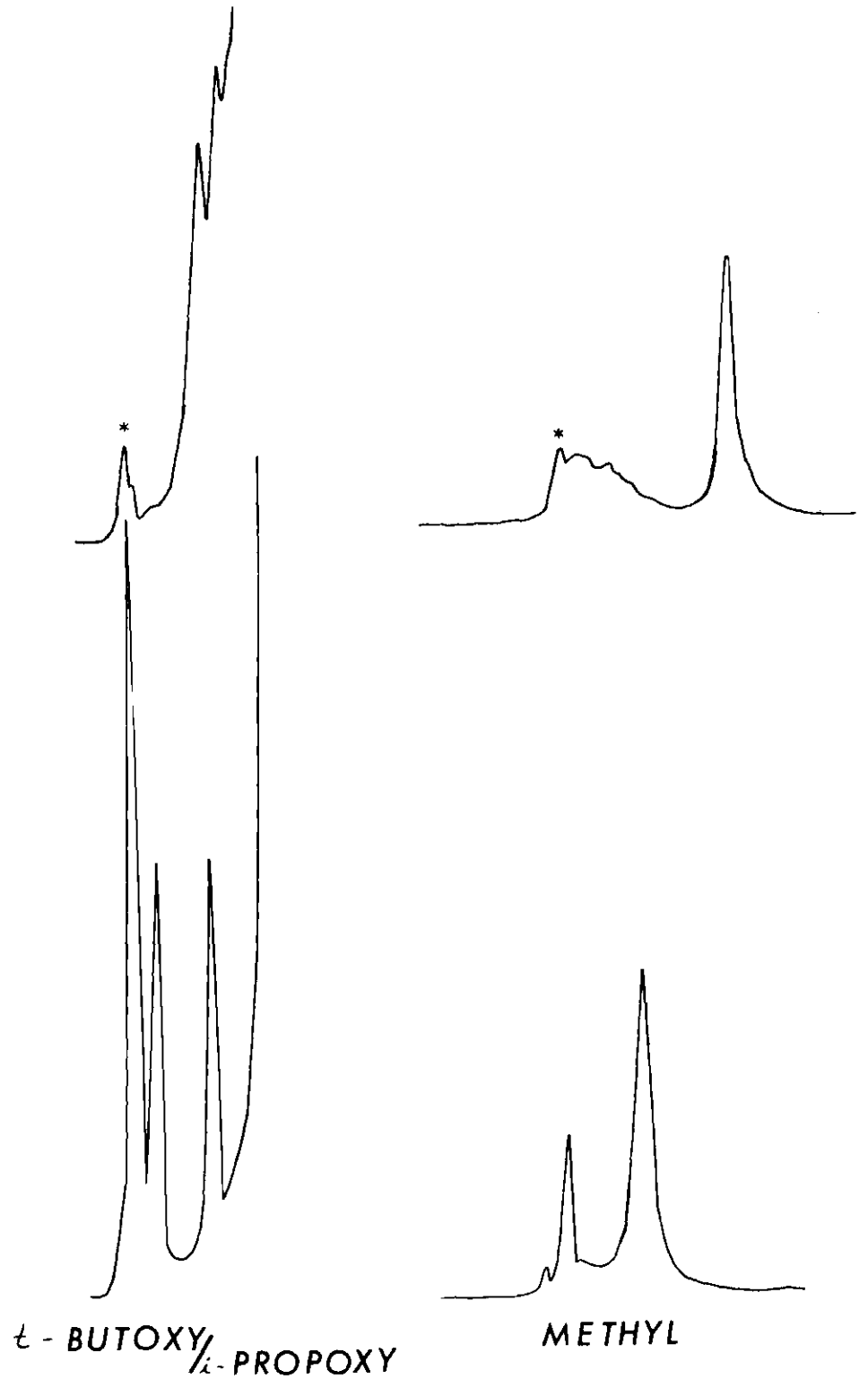


Figure 12. Ambient Temperature PMR Spectra of t-Butoxy(methyl)magnesium, Top; and Mixed t-Butoxy-/i-Propoxy-(methyl)magnesium, Bottom

contained only a very small amount of the thermodynamically preferred cubane form (top spectrum, Figure 12) because of the slow interconversion reaction, the mixed system (bottom spectra, Figure 12) contains a large percentage of t-butoxy and methyl groups in cubane sites (marked by *) of presumably mixed cubanes which are formed more rapidly than the pure t-butoxy(methyl)magnesium cubane tetramers. This experiment lends strong support to conclusions that i-propoxy(methyl)magnesium forms cubanes in diethyl ether and that these cubanes are kinetically labile.

n-Propoxy(methyl)magnesium

The behavior of n-propoxy(methyl)magnesium is similar to i-propoxy(methyl)magnesium in diethyl ether and tetrahydrofuran, but in benzene and toluene it appears to be more highly associated in a fashion similar to n-propoxy-, ethoxy- and methoxy-(alkyl)magnesium compounds reported by Coates (1).

When one mole equivalent of n-propanol was reacted with dimethylmagnesium in diethyl ether at low temperature and the solvent was removed in vacuo, unsolvated n-propoxy(methyl)magnesium was isolated in a form which is soluble in diethyl ether, tetrahydrofuran or benzene. The IR spectrum of this compound is the top spectrum in Figure 13. When heated in vacuo at 120 to 130°, an unrecoverable amount of white solid sublimed while the bulk of the sample yellowed. The IR spectrum of this decomposition product is the bottom spectrum in Figure 13. As in the case of i-propoxy(methyl)magnesium, heating n-propoxy(methyl)magnesium results in major structural changes and apparent decomposition.

The PMR spectra of n-propoxy(methyl)magnesium (Table 1) suggest

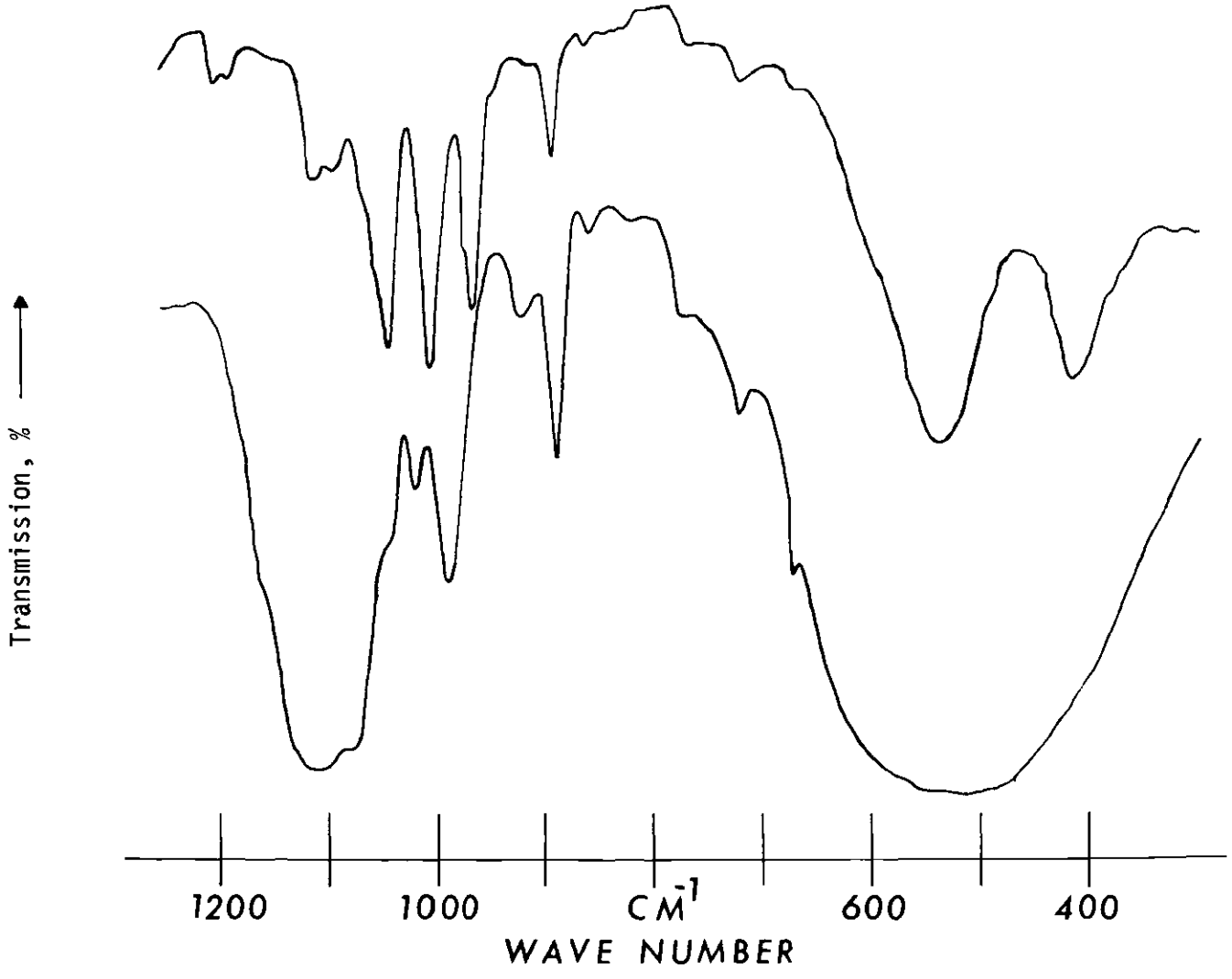


Figure 13. Infrared Spectra of n-Propoxy(methyl)magnesium, Top; and Its Decomposition Product when Heated to 130°, Bottom

that its composition in diethyl ether and tetrahydrofuran are different since in diethyl ether the chemical shift of the methyl group is in the region where cubane tetramers and/or bridging methyls of linear polymers absorb while in tetrahydrofuran the chemical shift is in the region expected for terminal methyl sites (Table 1). The molecular association results in these solvents (Appendix 3) also suggest compositional changes since in diethyl ether i = 4.31 ± 0.08 at 0.539 m and only decreases to i = 3.54 ± 0.41 at 0.076 m while in tetrahydrofuran i = 2.30 ± 0.03 at 0.426 m and decreases only to i = 1.93 ± 0.08 at 0.111 m. These results indicate that the preferred structures in diethyl ether solution are the cubane and linear polymers while the dimer(s) predominates even at relatively high concentration in tetrahydrofuran. Nackashi (2) has studied the low temperature PMR spectrum of n-propoxy-(methyl)magnesium in diethyl ether and has found that the 11.33τ signal observed at room temperature dominates the spectrum at as low as -110° though minor signals are resolved at 11.28 and 11.61τ. However, unlike the original study (2), the predominant signal is currently believed to be due to a cubane tetramer rather than bridging sites in linear polymers.

In benzene the molecular association of n-propoxy(methyl)magnesium was found cryoscopicly to be in the range i = 7 to 9 in the concentration range 0.209 to 0.324 m (Appendix 3). This result is similar to the observations of Coates and co-workers (1) who observed that n-propoxy(ethyl)magnesium, ethoxy(i-propyl)magnesium and methoxy(i-propyl)magnesium all had molecular association values in the range i = 7 to 9 in benzene. Recently, it has been suggested (10) that these

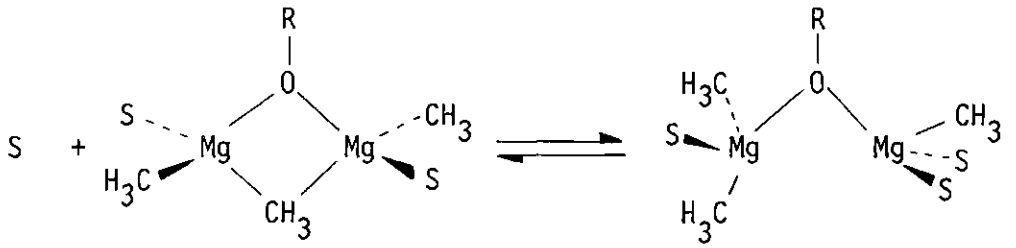
compounds may have a heptameric structure similar to VII. Coates reports that the alkyl and alkoxy PMR signals of some of the compounds he studied are split into unexplained doublets. However, three signals in the ratio 3:3:1 are expected for structure VII and have been observed in some aluminum-nitrogen analogues (10,11). Also, no unexplained splittings were reported for n-propoxy(ethyl)magnesium. The methyl PMR signal of n-propoxy(methyl)magnesium studied here is a sharp singlet at room temperature (Table 1) and no additional signals were observed at as low as -70° in toluene. However, the PMR signal of the methyl group of the n-propoxy group is more complex than observed in other solvents or for n-propanol itself. From the current studies, little can be added to the understanding of the structure of the alkoxy(alkyl)magnesium compounds which show high degrees of association, e.g., i = 7-9. As in the aluminum-nitrogen system, x-ray crystallographic results will probably be required to clear up this enigma.

Alkoxy(methyl)magnesium/Dimethylmagnesium Systems

In the preceding paragraphs, only new results obtained during these studies of the alkoxy(methyl)magnesium/dimethylmagnesium systems have been discussed. Because of the interest in mixed alkoxy-alkyl bridge systems and the fact that current results throw new light on prior art, it is worthwhile to state explicitly the current view of existing data.

In the cases cited previously (2,17), namely "$CH_3MgOR/(CH_3)_2Mg$" where the RO group is $(C_6H_5)_2CH_3CO$, $(CH_3)_3CO$, $(CH_3)_2HCO$ or $CH_3CH_2CH_2O$, molecular association results and low temperature PMR studies are

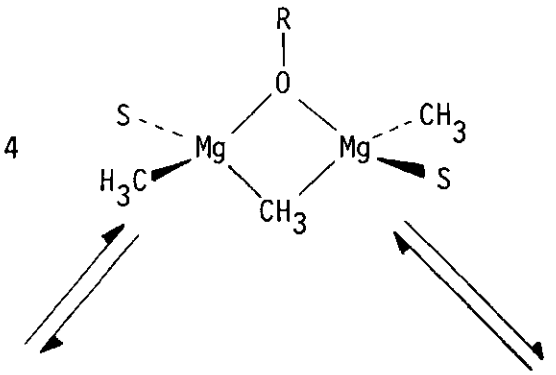
reported from which it is concluded that in each case the system can be represented by the equilibrium between mixed bridged and half bridged compounds.



Reexamination of these results suggests that they can be easily interpreted to fit other schemes and that in some cases the results are not at all consistent with the suggested equilibrium. However, the objections stated here are directed at the interpretation of results rather than the conclusions because it can be shown, in at least some cases, that the previous conclusions are essentially correct.

First, it appears that the prior art (2,17) repeatedly employs a questionable argument as "proof" of the formation of a complex between dimethylmagnesium and the alkoxy(methyl)magnesium compounds. For example, in reference 2 on pages 48, 55, 71 and 93 and in reference 17 on page C3, it is stated that the stoichiometric addition of Me_2Mg to . . . [MeMgOR] . . . results in the formation of a complex in solution, . . . [MeMgOR·Me_2Mg] . . . , as determined by the measurement of its molecular association. Ebullioscopic results are then cited which are consistent with the formulation as "i = 0.90-1.06, m = 0.0196-0.098". Apparently the molecular association results alone are cited as proof of the structure. This argument can be easily shown to be weak or perhaps completely invalid.

Consider the equilibrium mixture shown below.



$$(ROMgCH_3)_4 + 4\,(CH_3)_2Mg\,2S \rightleftharpoons (ROMgCH_3)_4 + 2\,(CH_3)_4Mg_2 \cdot 2S$$

Calculations of the i-values expected for the extreme cases of the equilibrium show that the observed i-value is not particularly sensitive to the composition. If OR is $OC(CH_3)_3$,

$$M_{avg} = \frac{4(166)}{4} = 166 \qquad i = \frac{166}{166} = 1.0$$

$$M_{avg} = \frac{1(448) + 4(54)}{5} = 133 \qquad i = \frac{133}{166} = 0.8$$

or

$$M_{avg} = \frac{1(448) + 2(108)}{3} = 221 \qquad i = \frac{221}{166} = 1.3$$

Note that changes in solvation result only in changes in concentration which will be neglectable in dilute solution. Obviously, the experimental i-values, lying in the range 0.9 to 1.1 for the most part, do not furnish much basis to distinguish these systems. Thus, while the i-values are consistent with the structures cited in the prior art (2,17), it is probably not realistic to imply that the structure was defined by

the ebullioscopic measurements.

Furthermore, comparison of the previously discussed PMR spectra of "t-butoxy(methyl)magnesium·dimethylmagnesium" (reference 2, page 155, Figure 3; also see page 156, Figure 4) with the time dependent spectra of t-butoxy(methyl)magnesium/dimethylmagnesium in diethyl ether reported here (Figure 10; also see Figure 6) shows clearly that the sample previously studied had aged to the point where only dimethylmagnesium and cubane t-butoxy(methyl)magnesium were present in solution. In support of the above arguments about the unreliability of i-values, note that the i-value reported for this sample was "i = 0.975-1.04, m = 0.104-0.301". Clearly, the prior art on this system is misinterpreted. However, as pointed out in the current discussion of Figure 10, the low temperature PMR spectra of kinetic t-butoxy(methyl)magnesium in the presence of a mole of dimethylmagnesium, the data suggest that in the absence of the cubane tetramers the conclusion reached in the prior art is very likely to be correct.

The implications of current results with regards to the other $ROMgCH_3/(CH_3)_2Mg$ systems studied previously (2,17) must be considered for several cases. In the case where RO is $(C_6H_5)_2CH_3CO$, formation of cubane tetramers has not been observed under these conditions and little tendency to form higher linear polymers has been displayed. Thus, the description originally proposed by Nackashi and Ashby (17) must be correct. In the cases where RO is i-propoxy or n-propoxy and the cubane $\rightleftharpoons$ kinetic product equilibrium is very rapidly established, the fact that in the kinetic t-butoxy(methyl)magnesium system the interaction with a mole of dimethylmagnesium was not strong enough to prevent

conversion to the cubane tetramer is important because it suggests that in the labile systems the mixed bridge complex may be less thermodynamically favored than the cubane. The PMR spectra of the n-propoxy- and i-propoxy(methyl)magnesium/dimethylmagnesium systems at -90° to -120° show a minor signal at about 11.30τ and a much more intense signal at about 11.55τ. The previous assignment of these signals to the mixed bridge $\rightleftharpoons$ half bridge equilibrium is logical. If this assignment is correct, then for these systems at low temperature, complex formation between dimethylmagnesium and the alkoxy(methyl)magnesium compounds is more favorable than conversion to cubane.

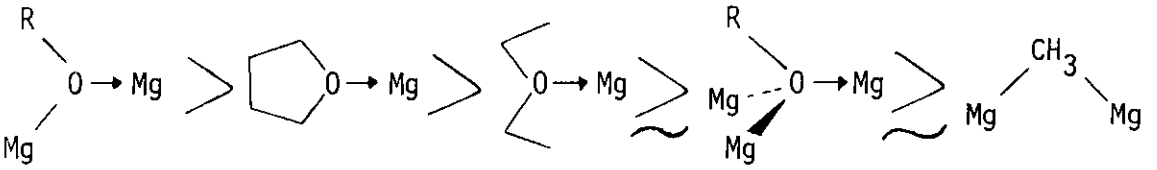
CHAPTER IV

CONCLUSIONS

In the following paragraphs, an attempt will be made to develop some useful concepts concerning the thermodynamic and kinetic relationships between the structures observed for alkoxy(methyl)magnesium compounds. The currently available data are insufficient to formulate a detailed, quantitative theory to predict the composition of any alkoxy(alkyl)magnesium compound in a given solvent, but the results described in the preceding chapters provide some important answers to questions raised by previous work in this field.

Thermodynamic Considerations

It has been shown that not only can alkoxy(methyl)magnesium compounds form a variety of stable structures (e.g., I-VII), but also that any particular alkoxy(alkyl)magnesium compound may prefer different structures under different conditions. The objective in this paragraph is to analyze the various bonding and non-bonding interactions found in these structures and to rank them in importance. Unfortunately, many of these interactions are of very nearly equal importance, so that small changes in the alkoxy group, the alkyl group or the solvent can have unexpectedly large effects upon the stability of a given structure. Some of the important bonding interactions can be ranked roughly as shown below:



An indication of the scale and precision of this ranking can be found in the estimation of $-\Delta H$ for coordinate bond formation between tetrahydrofuran and a typical magnesium atom as 12 to 15 kcal/mole, and between diethyl ether and a typical magnesium atom as 9 to 12 kcal/mole depending upon such things as the steric bulk and electronegativity of other groups coordinated to the magnesium atom. The relative values for the numerical scale are based on the observed heat of replacement of diethyl ether coordinated to diethylmagnesium by tetrahydrofuran. Smith and Becker (19) cautiously write the reaction as

$$(Et_2Mg \cdot xEt_2O)_1 + y\ THF \rightleftharpoons (Et_2Mg \cdot yTHF)_1 + x\ Et_2O$$

with $\Delta H(25°)_{obs} = -4.6$ kcal/mole, but the main reaction can be approximated by $x = y = 2$ for this system. Thus, the reaction

$$R_2Mg \cdot S + S \rightleftharpoons R_2Mg \cdot 2S$$

is expected to liberate about 2 to 3 kcal/mole more heat when S = THF than when S = Et_2O. It is less obvious how the absolute values for the numerical scale were derived. The rationalization begins with the approximation of another one of Smith and Becker's results by the equation

$$MgBr_2 \cdot 2Et_2O + 4\ THF \rightleftharpoons MgX_2 \cdot 4THF + 2\ Et_2O$$

to which the result observed for replacing diethyl ether with tetrahydrofuran on magnesium bromide ($\Delta H(25°)_{obs}$ = -19.1 kcal/mole) is applied. This reaction can be replaced by two equations

$$MgBr_2 \cdot 2Et_2O + 2\ THF \longrightarrow MgBr_2 \cdot 2THF + 2\ Et_2O$$

$$MgBr_2 \cdot 2THF + 2\ THF \longrightarrow MgBr_2 \cdot 4THF$$

Using the previous arguments, replacement of two Et_2O molecules by two THF molecules can be approximated by 5 kcal/mole. By subtraction the second reaction can be assigned an enthalpy of ∿14 kcal/mole (19-5=14), which suggests ∿7 kcal/mole for the reaction

$$MgBr_2 \cdot 3THF + THF \longrightarrow MgBr_2 \cdot 4THF$$

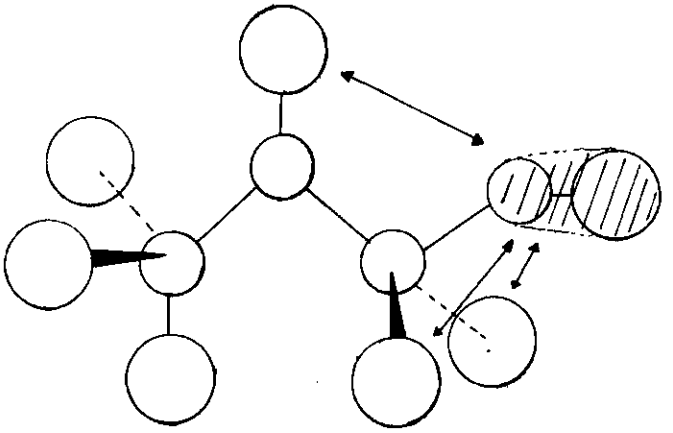
It is expected that the reaction

$$MgBr_2 \cdot THF + THF \longrightarrow MgBr_2 \cdot 2THF$$

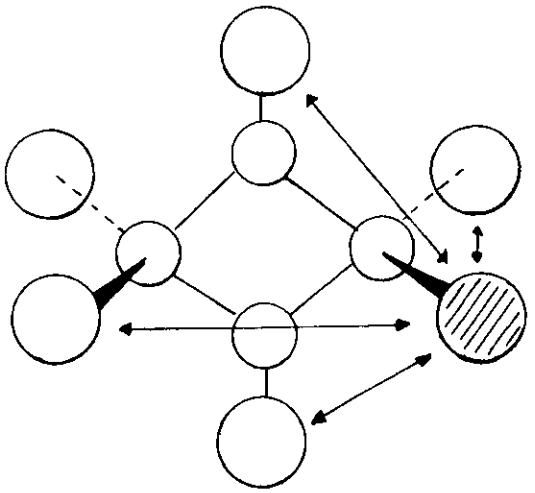
will liberate "appreciably" more heat (see arguments on page 52 of Part I of this thesis). Hence, with some "hand waving", the intuitive value of 12 to 15 kcal/mole for THF and 9 to 12 kcal/mole for Et_2O coordinate bond formation to four coordinate magnesium can be rationalized. This ranking is compatible with the observed preference for solvated dimers (e.g., I, II, III) in tetrahydrofuran solution, while in diethyl ether solution structures with methyl bridge bonds and $\mu_3$alkoxy bridges are observed (e.g., linear polymers, cubanes).

Steric interactions are very hard to localize or attribute to a single group. The effect of any steric crowding will be partially

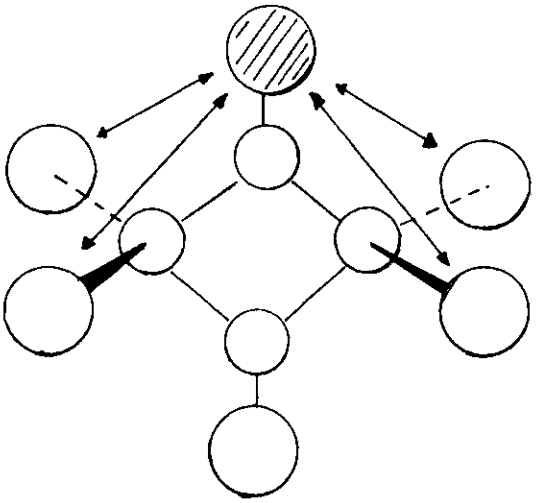
compensated for by changes in bond length and bond angles, i.e., conformational changes, throughout the molecular framework. For simplicity, consider the organic groups and the coordinated solvent molecules as space-filling substituents on the basic magnesium-oxygen skeleton. It is probably worthwhile to categorize these groups as "isotropicly bulky" or "anisotropicly bulky". An isotropicly bulky group is one such as the methyl or t-butyl group which cannot appreciably reduce its bulk in any direction by simple rotations around single bonds; while an anisotropicly bulky group such as i-propyl or n-propyl or a coordinated ether molecule can adopt a conformation of minimum steric interaction by simple rotations around single bonds. With these simplifications, some of the important steric interactions in structures I, II, III and V are shown below. These structures, in which only steric features are represented, correspond to the structures of the same numbers found on pages 119 and 120. The vagueness of these qualitative diagrams emphasizes the uncertainties in the analysis of steric interactions. It is clear that a full interpretation of steric effects must also take into account many subtle changes in conformation of the various structures.



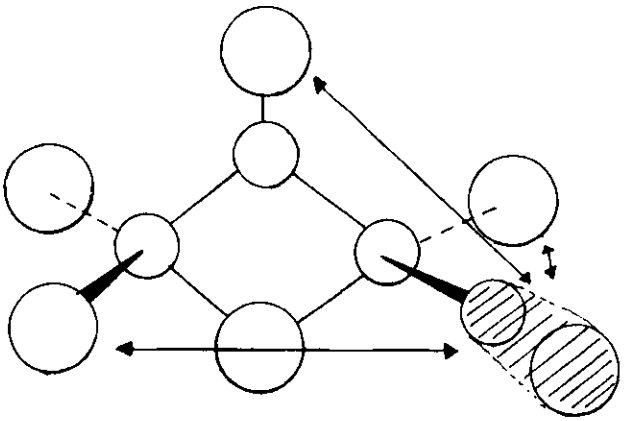
I



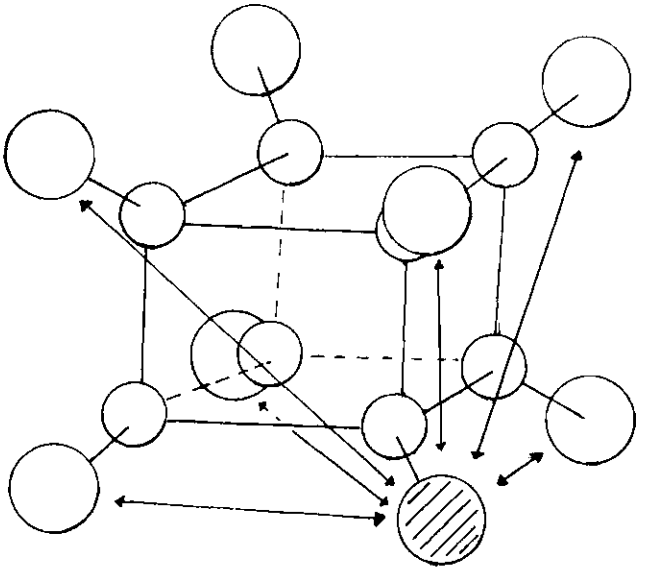
II
(interactions involving
terminal substituent)



II
(interactions involving
bridge substituent)



III



V

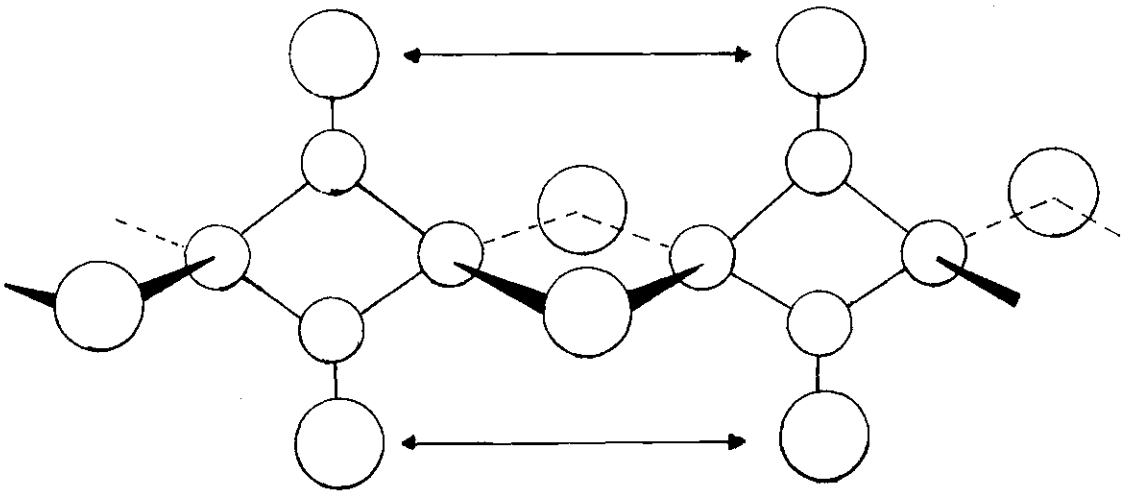
It can be generalized that as the substituents on the magnesium oxygen skeleton of these structures become more bulky, the steric interactions noted above become more unfavorable and the structures become less stable. However, their relative stabilities and hence the preferred composition in solution of a specific alkoxy(alkyl)magnesium compound change with increase in steric bulk of the substituents primarily because some structures accommodate the increased steric bulk more readily than others. Models are helpful in judging the ability of the structures shown above to accommodate the steric bulk of the substituents but the simple stick-and-ball drawings are almost as accurate in depicting the important interactions.

Few good predictions about the effect of steric bulk of the substituents on the thermodynamically preferred structure are possible based on these models and drawings. Coates (1) has argued that the

failure to obtain cubane type molecules with bulky alkoxy groups such as 1,1-diphenylethoxy can be accounted for by the necessity of bringing the bulky groups together on the same side of the four membered rings which form the faces of the cubane. The same argument accounts for the failure to obtain linear polymers. Even with the limitations of the current level of approximation, this argument appears to be sound because the interaction to which Coates calls attention (the interaction of the alkoxy groups across the diagonal of the four membered rings) is probably nil even for very large alkoxy groups in the dimers of type II. In the cubanes of type V the repulsive forces diagonally across the faces of the cubanes undoubtedly increase as the substituents on the magnesium-oxygen skeleton. However, it should also be noted that there are significant interactions along the edges of the cubane V which are minimized though not eliminated in the dimer II.

Nackashi and Ashby (2,17) have introduced the concept that an equilibrium between structures II and III can become important when the alkoxy group is very bulky. It follows that the equilibrium would also involve structure I when the solvent is capable of breaking the alkyl bridge bond of structure III. The flexibility of I should provide the most ability to accommodate bulky alkoxy groups, and III can probably accommodate bulky alkoxy groups better than II. However, the evidence suggests that dimer II is heavily favored even when the alkoxy group becomes quite bulky.

In the formation of linear polymers based on dimer II or dimer III, interactions between alkoxy groups in adjacent four membered rings probably play an important role in polymer stability.



polymer II

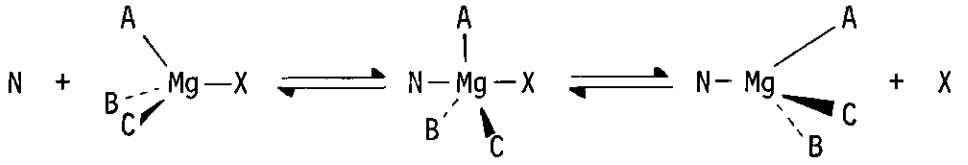
These interactions may account for the observation that the kinetic form of t-butoxy(methyl)magnesium associates beyond the dimer stage in concentrated diethyl ether solution while 1,1-diphenylethoxy(methyl)-magnesium does not tend to associate beyond the dimer under similar conditions.

The preferred solution composition of a specific alkoxy(alkyl)-magnesium compound is very hard to predict in detail because it depends upon small but decisive energy differences between large and imprecisely known total energies of attraction and repulsion. On the other hand, basic knowledge of the solvation processes allow the prediction of the types of structures which may be favored in a particular solvent.

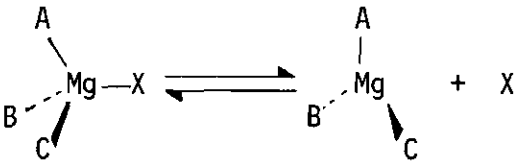
Kinetic Considerations

The variation in rates of exchange reactions and equilibrium establishing reactions shown by the alkoxy(alkyl)magnesium compounds is remarkable. These effects appear to be due to the ability of sterically

bulky groups to prevent nucleophilic attack on magnesium by the solvent which often assists in bond breaking reactions. In general, this effect is believed to be similar to the difference between S_N2 and S_N1 reactions generally encountered in organic chemistry.



S_N2 - Associative displacement

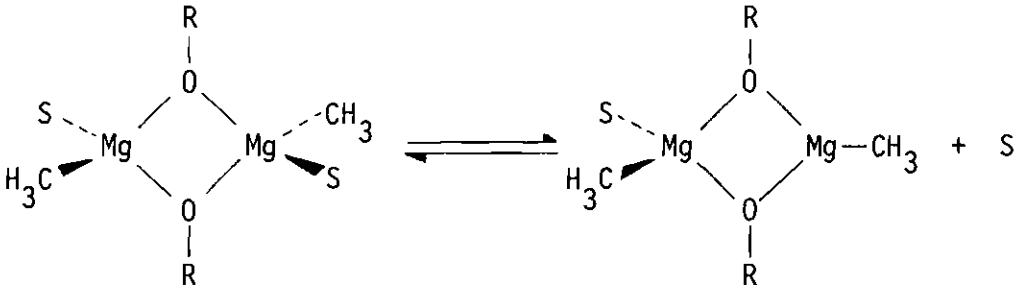


S_N1 - Dissociative displacement

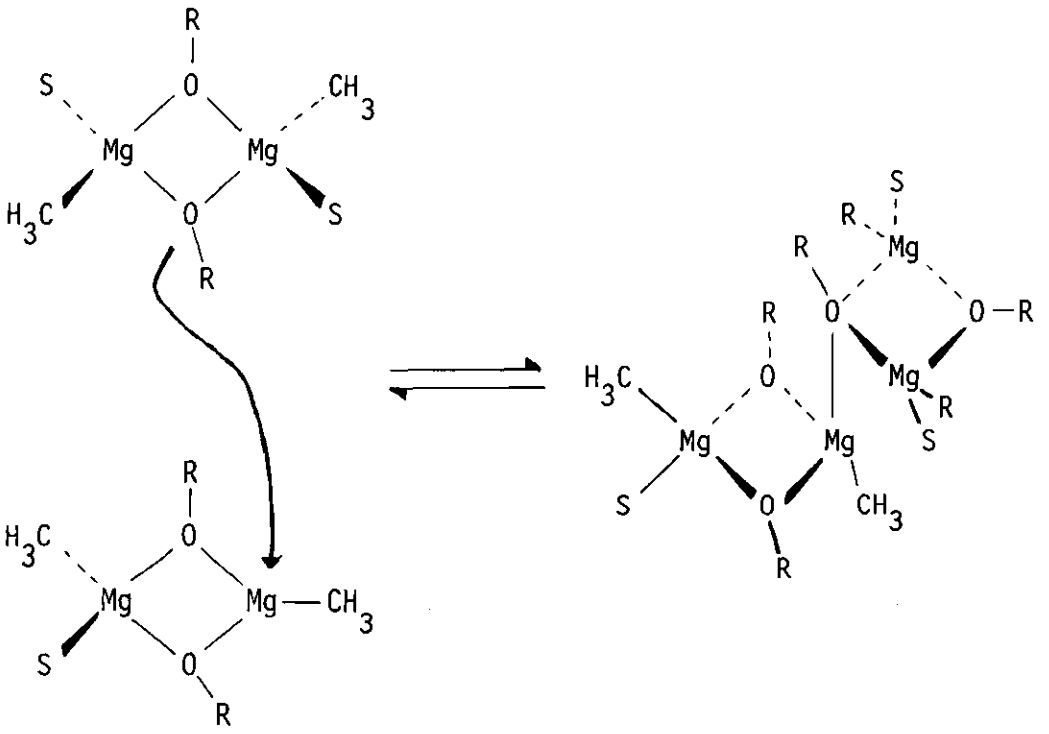
Unlike the familiar S_N2 displacements at carbon, the pentacoordinate associative intermediate with magnesium as the central atom is probably not a transition state in most cases because magnesium is a second row element and coordination numbers greater than four are common. Unfortunately, considerably more work will need to be done before a detailed picture of these processes can be drawn.

A possible sequence of steps for the dimer $\rightleftharpoons$ cubane interconversion is suggested below. It should be remembered that dimer II is simultaneously in equilibrium with other dimers (II $\rightleftharpoons$ I $\rightleftharpoons$ III) and linear polymers.

Step 1, Desolvation of the Dimer:



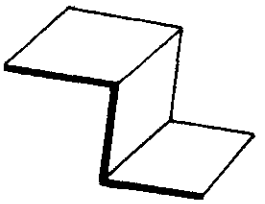
Step 2, Attack by a Second Dimer to Form a μ_3 Oxygen Bridge:



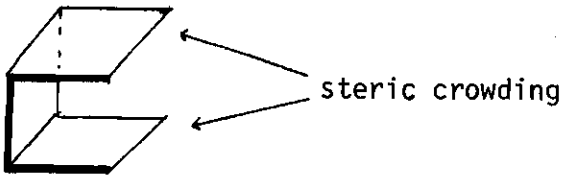
Steps 1 and 2 are probably quite rapid. In cases where the alkoxy group is not particularly bulky, Step 1 and 2 may be combined as a concerted displacement of solvent by the μ_2 alkoxy group of a second dimer.

Step 3, Formation of a Second μ_3 Oxygen Bridge:

For simplicity, the question of whether or not loss of solvent proceeds or is concerted with formation of a second μ_3 oxygen bridge will not be considered explicitly. At this stage it is believed that either mechanism would be rapid even for systems with bulky alkoxy groups. There are two basicly different ways to form the second μ_3 oxygen bridge. The reaction requiring the least steric interaction results in a "modified" cubane tetramer with a skeleton shaped like a "Z".



Considerably more steric interaction is encountered when a "C" shaped skeleton is formed.

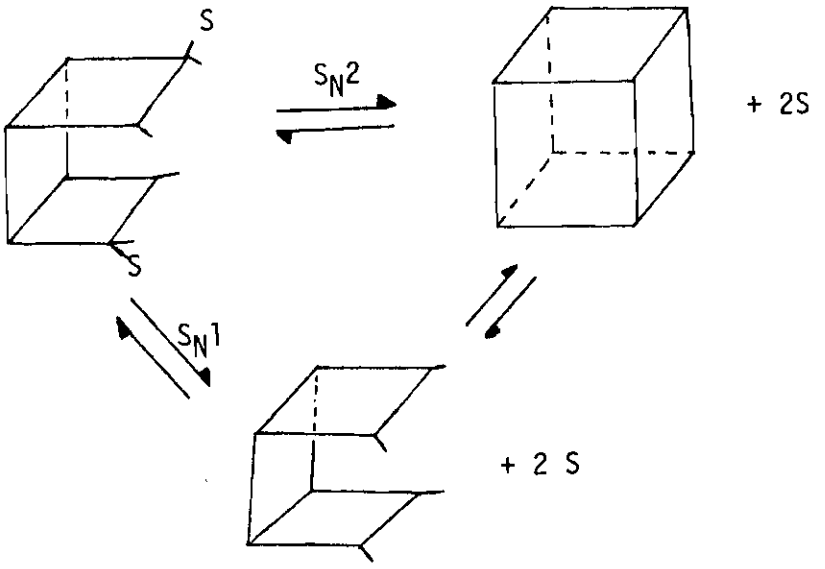


It would seem that for non-bulky alkoxy groups the "C" skeleton, modified cubane would be almost as easily achieved as the "Z" skeleton. However, the "C" conformation should be more difficult to achieve as the alkoxy groups and solvent molecules become more bulky.

Step 4, Formation of the Third and Fourth μ_3 Oxygen Bridges from the "C" Skeleton Modified Cubane:

It seems likely that closure of the "C" skeleton to the unsolvated cubane involves nearly simultaneous formation of the third and fourth μ_3 oxygen bridges. This is probably the point at which the large activation energy for dimer $\rightleftharpoons$ cubane interconversion for t-butoxy(methyl)magnesium is developed. For the less bulky systems, loss of solvation, as the solvated "C" skeleton modified cubane closes to the unsolvated cubane tetramer, is probably assisted by considerable development of the last two μ_3 oxygen bridge bonds. On the other hand, models suggest that for the t-butoxy(methyl)magnesium, the coordinated solvent molecules must depart completely before there is sufficient room to bring the magnesium and μ_2 oxygen atoms within bonding distance. The enthalpy for loss of two moles of solvent without compensating oxygen bridge formation is expected to be on the order of 20 to 25 kcal/mole. This estimation of the activation energy in the proposed mechanism is consistent with the observed rate of cubane $\rightleftharpoons$ dimer interconversion in t-butoxy(methyl)magnesium.

Formation of the third and fourth μ_3 oxygen bridges can either be concerted with loss of solvent (S_N2) or follow loss of solvent (S_N1), depending upon the bulk of the alkoxy group.



For the compounds with less bulky alkoxy and/or alkyl groups, solvent assistance in the initial step of breaking the μ_3 oxygen bridges of the cubane can greatly reduce the energy required to go to the modified cubane (Figure 14).

The overall sequence is summarized in Figure 15. Two pathways are shown for interconversion of "Z" and "C" skeleton modified cubanes. It is possible to speculate that the pathway involving conformational changes of a six membered ring fused to a four membered ring could be a mechanistic point of departure for formation of more complex cage oligomers such as structure VII on page 121.

It is also notable that bridge-terminal exchange in the system of kinetic t-butoxy(methyl)magnesium in diethyl ether is exceptionally slow. Separate signals are observed for bridging and terminal methyl sites at +40° in the PMR spectrum. For example, see Figures 4 and 6. A reasonable explanation of this phenomenon can be based on the same

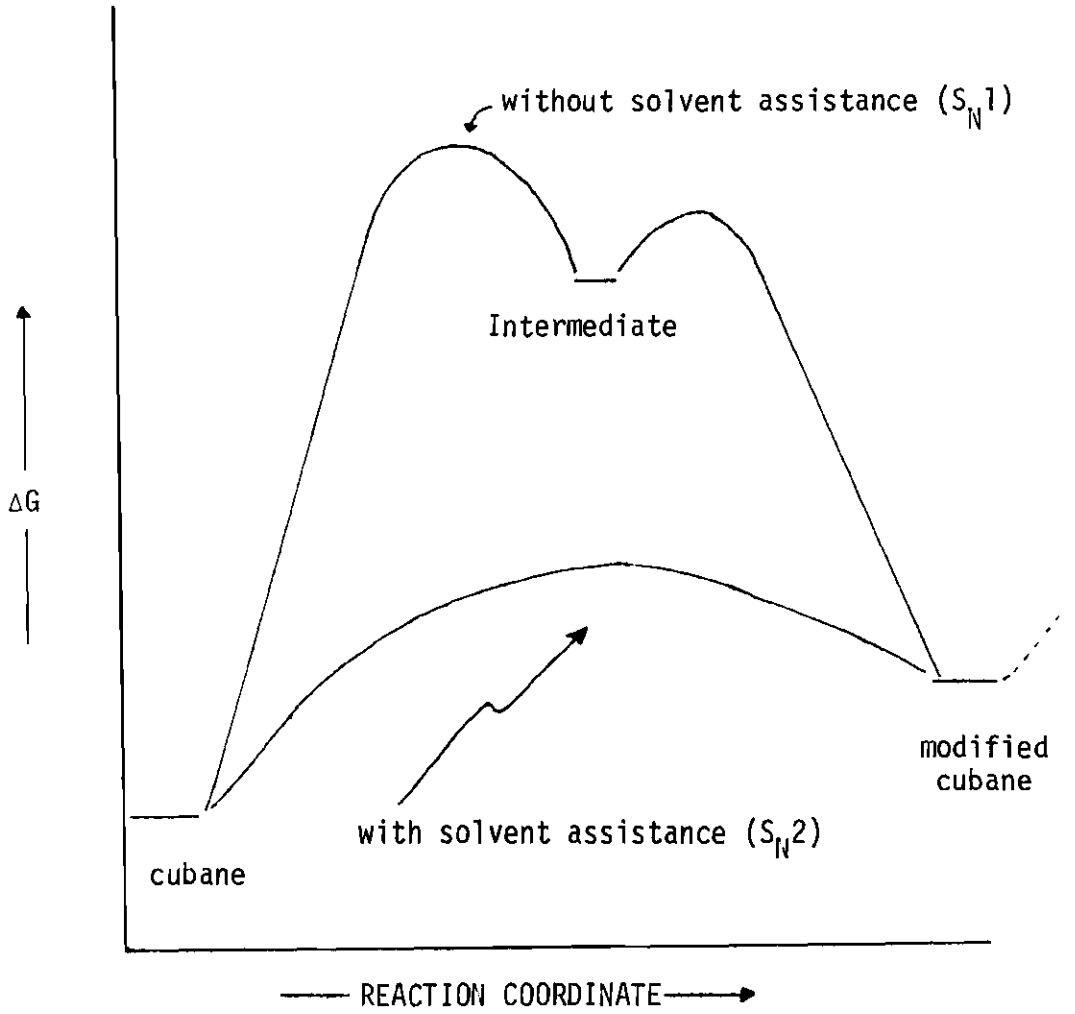


Figure 14. Hypothetical Free Energy Profile for First Stages of Cubane to Dimer Conversion

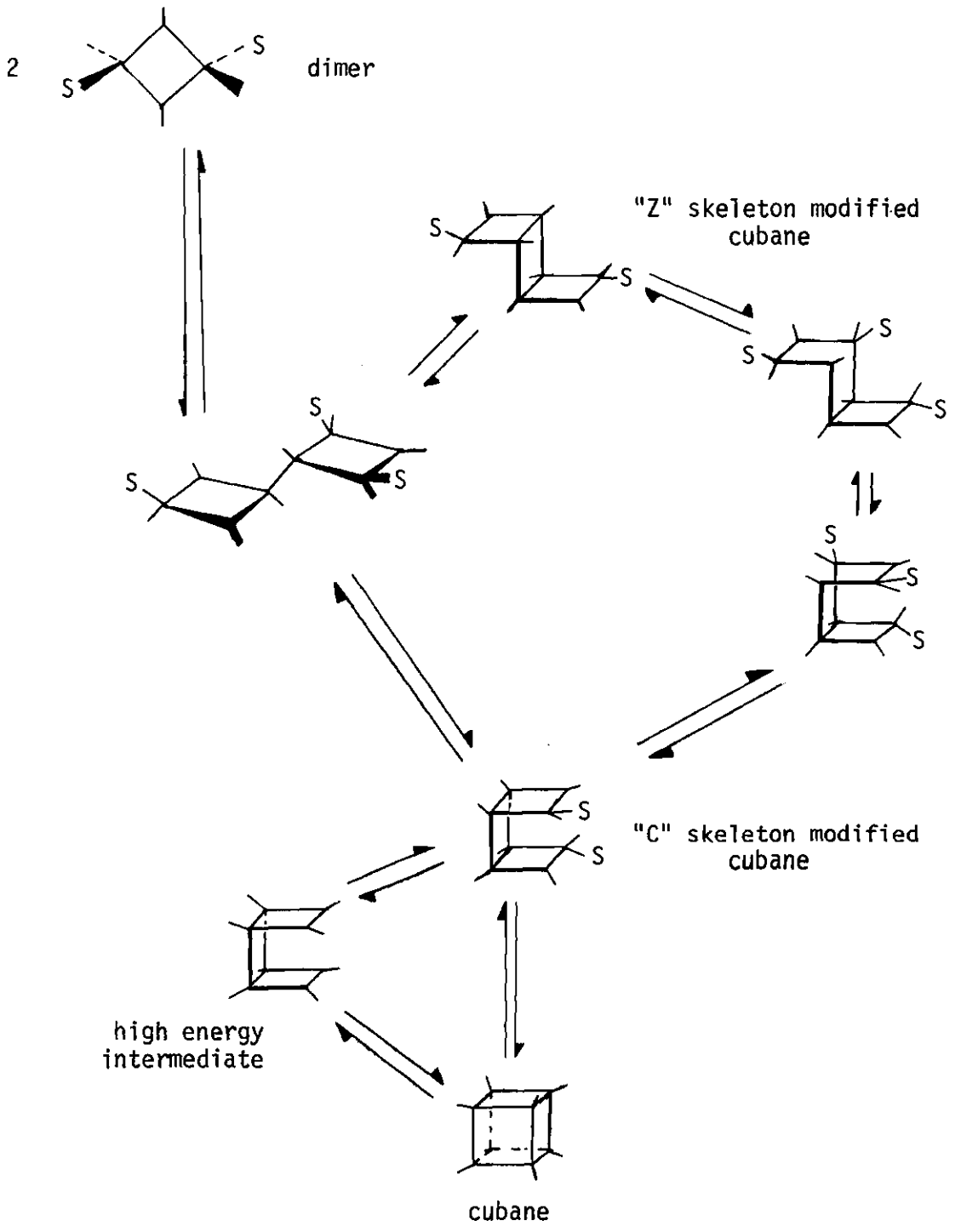
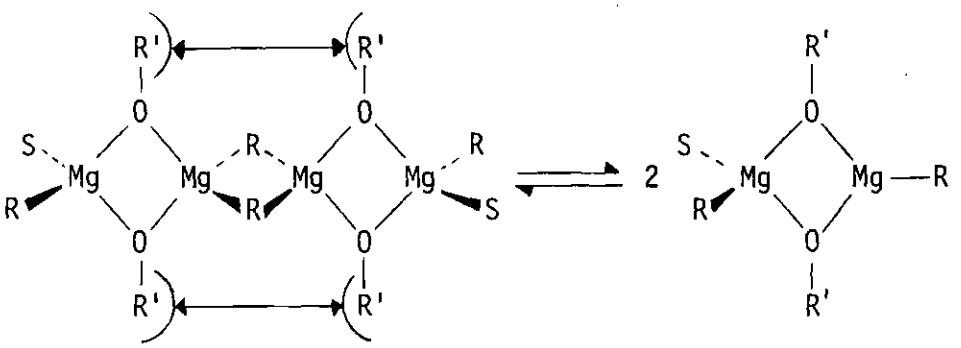
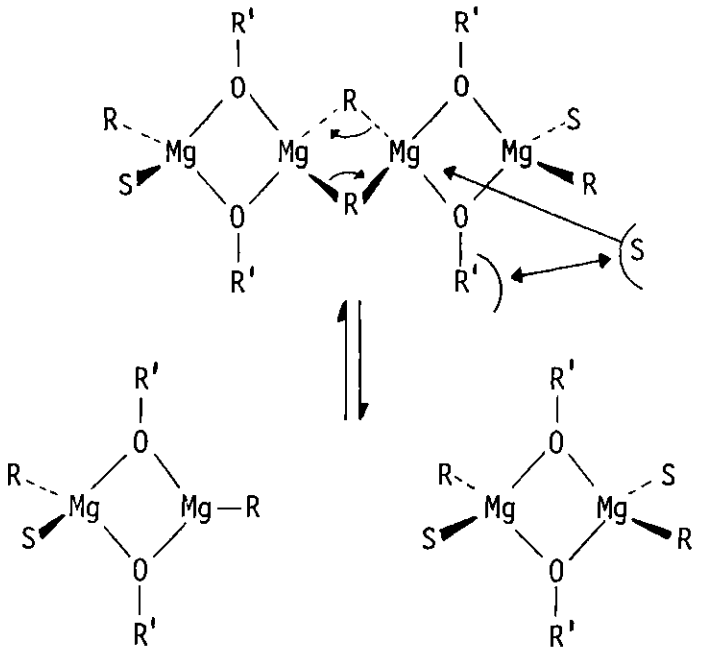


Figure 15. Suggested Overall Mechanism for Dimer to Cubane Interconversion

hypothesis of solvent assisted bond breaking invoked to rationalize the inertness of the stericly crowded cubane tetramers. If the bridge-terminal exchange process were not solvent assisted, steric crowding of the polymer ought to enhance the rate of exchange provided the exchange mechanism is dissociative.



On the other hand, if the solvent assisted mechanism is generally preferred over the unassisted dissociation of the bridge bonds, steric crowding can interfere with the nucleophilic displacement of the bridging group by the solvent in an S_N2 fashion.



In conclusion, it is obvious that the rationales discussed in this chapter are little more than speculation considering the small amount of available data. Actually, this area of chemistry is still very much in the exploratory phase and the scope of the chemical problem is just beginning to take shape. The chief justification for indulging in speculation of the type found here is that while it may well be incorrect, in part if not in whole, it will stimulate experimentation which will ultimately answer the important questions concerning the structures, thermodynamics and kinetics of these compounds.

APPENDIX 1

OPERATING RANGE OF THE EBULLIOSCOPIC APPARATUS

When using an ebullioscopic apparatus there is a preferred range of volume (mass) of solution for achieving and maintaining good thermal equilibrium within the system. However, there is little data available to judge the magnitude of the effect of variations in the amount of solution upon the experimentally measured boiling point. In Figure 16, the results of a study of the effect of the amount of solvent on the apparent degree of association (i-value) of benzophenone in diethyl ether at two concentrations is illustrated. The ebullioscopic apparatus use was described by Walker and Ashby (15). If too little solvent is used, the Cottrell pump does not work, the apparatus equilibrates slowly, and more importantly, the thermometer bulb is bathed only by condensing pure solvent. The pure solvent condenses at lower temperature than the temperature of the boiling solution. If so much solution is used that the thermometer touches the liquid, the larger values of ΔT_{bp} are observed, suggesting superheating of the solution (i.e., the observed temperature is higher than the thermodynamically meaningful temperature of the boiling solution in equilibrium with the vapor phase.)

For apparatus of the types described by Walker and Ashby (15) and used in these studies, this effect can amount to more than 0.05 degrees. When ΔT_{bp} is large relative to 0.05 degrees, the calculated i-values are insensitive to the amount of solution used, but when ΔT_{bp}

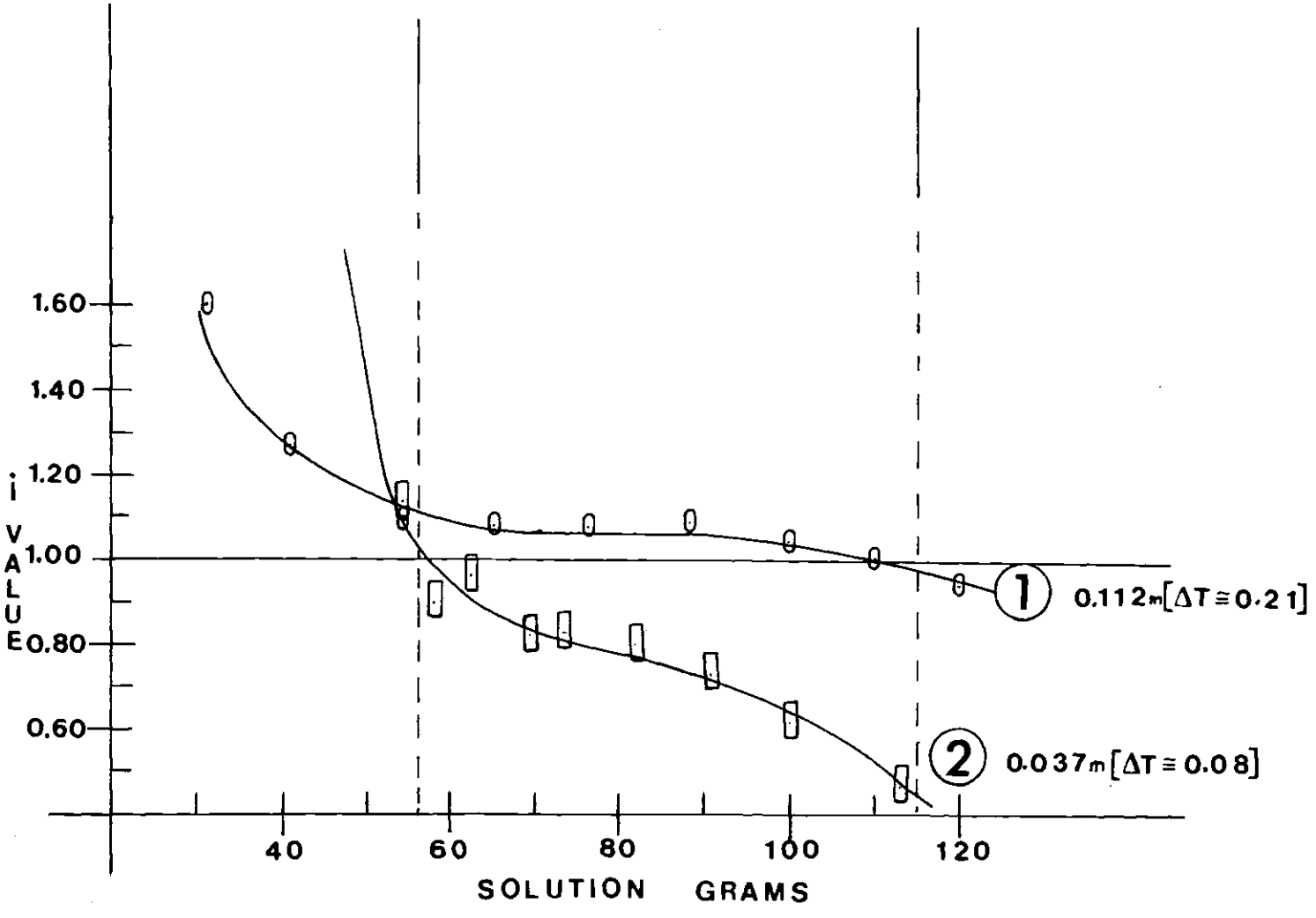


Figure 16. The Effect of the Amount of Solution on the Calculated i-Value for Benzophenone Solutions in Diethyl Ether

is on the same order of magnitude as 0.05 degrees the effect can be great enough to give misleading results. In Figure 16, the normal operating range (between 56 and 114 gr of solution for the particular apparatus used) is indicated by the dotted lines. In the case of the 0.112 m solution with $\Delta T_{bp} \simeq 0.21$ degrees, the observed i-value is not much affected by the amount of solution. However, for the 0.037 m solution with $\Delta T_{bp} \simeq 0.08$ degrees, the calculated i-value goes below 0.5 when the superheating effect is greatest. Notice that due to an inherent experimental uncertainty of ±0.005 degrees in the temperature measurement, the uncertainty in the calculated i-value is greater when ΔT_{bp} is small. It should also be noted that the boiling point of pure solvent (from which ΔT_{bp} was calculated) was determined with 65 gr of solvent in the apparatus.

It is believed that one of the causes of the effect just described is the hydrostatic pressure of the standing solution. In the apparatus described by Walker and Ashby (15), the solution is heated at the very bottom. Thus, the pressure at the point where boiling is initiated is equal to the pressure of the atmosphere above the solution which is read on the manometer plus the hydrostatic pressure of the liquid. In the normal operating range, the height of the column of liquid changes by as much as 80 mm. (The total height of the column of liquid can be as much as 180 mm.) The density of ether solutions is on the order of 0.75 gr/cc as compared to 13.6 gr/cc for mercury. The ratio of densities is 5.5×10^{-2} so a change in hydrostatic pressure of 80 mm of ether solution is the same as a change of 4.4 mm of Hg. For diethyl ether and tetrahydrofuran dT_{bp}/dP is about 0.04 deg/torr at

760 torr (20). So the hydrostatic effect would be expected to increase the temperature at which boiling is initiated by about 0.18 degree when the amount of solution is changed from the minimum to the maximum of the normal range provided the overhead atmospheric pressure is kept constant. Since the observed effects are usually in the range 0.05 to 0.10 degree, some equilibration of temperature is occurring. It should be noted that the total effect due to the total column of solution can be as much as 0.4 degree if the apparatus is fully loaded. These calculations and experimental results (Figure 16) point out the need for good insulation of the apparatus to reduce thermal gradients from the top to the bottom of the solution and the desirability of measuring boiling points of pure solvent and solution using the same amount of each in the apparatus.

APPENDIX 2

EXPERIMENTAL UNCERTAINTY IN MOLECULAR ASSOCIATION STUDIES

In order to correctly interpret quantitative experimental data, it is necessary to not only know the most likely value of a variable but also to know how accurately that value is determined. The theory and practice of molecular association studies via colligative property measurements have been recognized as useful research tools since the nineteenth century. However, the theoretical and practical limitations of the technique are often underestimated or totally ignored by chemists interested only in using the technique as a tool. In this appendix, attention will be called to some general experimental limitations of apparatus used in organometallic research. All solutions will be assumed to behave ideally.

The calculation of apparent molecular weights and i-values involves four experimental measurements, though only three are commonly made in most experiments. Measurement of the mass of solute, mass of solvent and change in the normal freezing or boiling point of the solvent must be made for each calculated molecular weight. However, the freezing point or boiling point variation constant of the solvent is actually a parameter which is often determined experimentally rather than calculated from theory (21). For example, in the case of benzene, the K_{fp} calculated from the normal freezing point and heat of fusion is 5.12 deg·kg·mole^{-1} while the emperically determined value of 4.90 deg·kg·mole^{-1} seems to

give more acceptable calculated molecular weights for "standard" compounds (22). This discrepancy is about 5%.

The weight of solvent and solute can be potentially determined to extreme accuracy with high precision balances. It is commonly possible to "read" mass to ±0.0001 gr. With mass of solute of about 1 gr and mass of solvent of about 100 gr the weighing error should be quite neglectable. However, experience with manipulation of syringes for the transfer of volatile solvents such as diethyl ether suggests that an error of about ±1% can be expected in both these weighings since the solute is usually handled in solution form. This error is still quite tolerable for most work.

The largest single source of experimental uncertainty is probably measurement of temperature. Several temperature measuring devices are commonly employed and there have been efforts to correct for shortcomings by careful experimental design. For example, Coates (1) reports the use of a differential ebulliometer with a 36-junction copper-constantan thermocouple. In a differential ebulliometer, errors due to pressure fluctuations and thermal lags are largely overcome. The precision of a non-differential setup is apt to be considerably lower due mainly to pressure effects. For example, for diethyl ether or tetrahydrofuran, dT_{bp}/dP at 760 torr is about 0.04 degrees/torr. Even precision manometers are only calibrated in torr and it is difficult to reproduce a pressure setting in a non-differential ebulliometer to better than ±0.1 torr. Thus the pressure adjustment itself can easily introduce a ±0.004 degree uncertainty in measured boiling points. Similarly, Beckman

thermometers are only calibrated in 0.01 degree increments and the estimation of a boiling or freezing point to the nearest 0.001 degree must have some subjective character.

It is concluded that citations of molecular weights determined by cryoscopic or ebullioscopic techniques by authors in the literature are usually quite glib. Authors and referees alike seldom challenge molecular association results, little reference to experimental technique is made and unwarranted faith is often invested in the calculated results.

For the results cited in this thesis, a good rule of thumb can be used to evaluate the experimental uncertainty in calculated molecular weights or i-values. Particularly in the case of cryoscopic measurements, error in temperature measurement is probably the most significant factor. Thus, the following equation is offered to estimate error in calculated i-values,

$$\delta i = i \frac{\delta \Delta T}{\Delta T} \quad ,$$

where $\delta \Delta T$ is estimated as 0.01 deg for cryoscopic measurements and 0.005 deg for ebullioscopic measurements. With these approximations, uncertainties in i-values are usually in the range of 1 to 10%.

APPENDIX 3

MOLECULAR ASSOCIATION DATA

t-Butoxy(methyl)magnesium (Kinetic Form) in Diethyl Ether

t-Butoxy(methyl)-magnesium (gr)	Ether (gr)	ΔT_{bp}	molality	i-value
2.839	62.051	0.215	0.406	3.79
2.839	75.593	0.200	0.334	3.34
2.839	89.181	0.190	0.283	3.02
0.385	73.474	0.046	0.047	2.03

t-Butoxy(methyl)magnesium (Kinetic Form) in Tetrahydrofuran

t-Butoxy(methyl)-magnesium (gr)	Tetrahydrofuran (gr)	ΔT_{bp}	molality	i-value
3.702	80.845	0.440	0.434	2.02
3.702	101.359	0.351	0.346	2.02
3.702	117.227	0.318	0.299	1.93

t-Butoxy(methyl)magnesium (Cubane Form) in Benzene

t-Butoxy(methyl)-magnesium (gr)	Benzene (gr)	ΔT_{fp}	molality	i-value
1.168	51.507	0.245	0.202	4.04
1.168	65.230	0.190	0.159	4.12
1.050	62.945	0.165	0.148	4.42

1,1-Diphenylethoxy(methyl)magnesium in Diethyl Ether

1,1-Diphenylethoxy-(methyl)magnesium (gr)	Ether (gr)	ΔT_{bp}	molality	i-value
3.916	57.522	0.245	0.288	2.35
3.916	68.585	0.215	0.241	2.25
3.916	78.832	0.198	0.210	2.12
3.916	89.704	0.188	0.184	1.97
3.916	100.220	0.170	0.165	1.95
1.407	63.551	0.080	0.0936	2.34
1.407	75.152	0.075	0.0791	2.12
1.407	86.384	0.068	0.0688	2.03
0.7161	60.564	0.046	0.0448	2.20

n-Propoxy(methyl)magnesium in Diethyl Ether

n-Propoxy(methyl)-magnesium (gr)	Ether (gr)	ΔT_{bp}	molality	i-value
3.280	61.886	0.250	0.539	4.31
3.280	75.225	0.220	0.443	4.03
3.280	91.300	0.198	0.365	3.69
2.299	85.870	0.140	0.272	3.90
0.610	55.633	0.060	0.111	3.73
1.141	65.660	0.104	0.177	3.41
0.509	68.121	0.043	0.076	3.54

n-Propoxy(methyl)magnesium in Tetrahydrofuran

n-Propoxy(methyl)-magnesium (gr)	Tetrahydrofuran (gr)	ΔT_{bp}	molality	i-value
3.640	86.721	0.405	0.426	2.30
3.640	105.771	0.328	0.350	2.33
3.640	118.852	0.303	0.311	2.24
1.041	94.915	0.127	0.111	1.93

n-Propoxy(methyl)magnesium in Benzene

n-Propoxy(methyl)-magnesium (gr)	Benzene (gr)	ΔT_{fp}	molality	i-value
1.451	45.474	0.235	0.324	6.8
1.451	61.052	0.135	0.241	8.8
1.451	70.522	0.118	0.209	8.7

i-Propoxy(methyl)magnesium in Diethyl Ether

i-Propoxy(methyl)-magnesium (gr)	Ether (gr)	ΔT_{bp}	molality	i-value
2.890	59.650	0.268	0.492	3.67
2.890	73.695	0.237	0.398	3.36
2.890	87.965	0.200	0.334	3.34
1.331	60.204	0.142	0.225	3.15
0.890	64.705	0.099	0.140	2.83

i-Propoxy(methyl)magnesium in Tetrahydrofuran

i-Propoxy(methyl)-magnesium (gr)	Tetrahydrofuran (gr)	ΔT_{bp}	molality	i-value
1.431	76.941	0.207	0.189	2.00
1.431	94.983	0.162	0.153	2.07
1.431	117.224	0.153	0.124	1.78

i-Propoxy(methyl)magnesium in Benzene

i-Propoxy(methyl)-magnesium (gr)	Benzene (gr)	ΔT_{bp}	molality	i-value
2.035	43.601	0.570	0.470	4.08
2.035	58.560	0.410	0.353	4.21
2.035	74.712	0.315	0.277	4.29

LITERATURE CITED*

(1) G. E. Coates, J. A. Heslop, M. E. Redwood and D. Ridley, J. Chem. Soc. (A), 1118 (1968).

(2) J. A. Nackashi, Ph.D. Thesis under E. C. Ashby at the Georgia Institute of Technology, Atlanta, Georgia (1974).

(3) P. Vink, C. Blomberg and F. Bickelhaupt, J. Organometal. Chem., 55, 57 (1973).

(4) D. Bryce-Smith and I. F. Graham, Chem. Comm., 559 (1966).

(5) P. T. Moseley and H. M. M. Shearer, Chem. Comm., 876 (1966).

(6) E. Weiss, H. Alsdorf and H. Kühr, Angew. Chem. Internat. Ed., 2, 328 (1963).

(7) H. M. M. Shearer and C. B. Spencer, Chem. Comm., 194 (1966).

(8) R. I. Botshkova, V. P. Golovatschev, E. P. Turevskaya and N. V. Belov, Dokl. Akad. Nank. SSR, 189, 1246 (1969).

(9) J. Toney and G. D. Stucky, J. Organometal. Chem., 28, 5 (1971).

(10) P. B. Hitchock, G. M. McLaughlin, J. D. Smith and K. M. Thomas, Chem. Comm., 934 (1973).

(11) K. J. Alford, K. Gosling and J. D. Smith, J. Chem. Soc. Dalton, 2203 (1972).

(12) G. E. Coates and K. Wade, "Organometallic Compounds, Vol. I, The Main Group Elements", Third Ed. Methuen & Company, London, 1967, p. 135.

(13) E. C. Ashby and R. D. Schwartz, J. Chem. Ed., 51, 65 (1974).

(14) E. C. Ashby and R. C. Arnott, J. Organometal. Chem., 14, 1 (1968).

(15) F. W. Walker and E. C. Ashby, J. Chem. Ed., 45, 654 (1968).

(16) H. O. House, R. A. Latham and G. M. Whitesides, J. Org. Chem., 32, 2481 (1967).

*Journal title abbreviations used are listed in "List of Periodicals" Chemical Abstracts (1961).

(17) J. A. Nackashi and E. C. Ashby, J. Organometal. Chem., 35, C1 (1972).

(18) G. E. Parris and E. C. Ashby, J. Amer. Chem. Soc., 93, 1206 (1971).

(19) M. B. Smith and W. E. Becker, Tetrahedron, 23, 4215 (1967).

(20) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry, Vol. 2, Organic Solvents", Third Ed., Wiley-Interscience, New York, N. Y., 1970, p. 204.

(21) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry, Vol. 2, Organic Solvents", Third Ed., Wiley-Interscience, New York, N. Y., 1970, pp. 48-52.

(22) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill Co., New York, N. Y., 1969, p. 160.

VITA

George Edward Parris was born on July 3, 1947 in Raleigh, North Carolina and subsequently attended public school in the suburb of Garner. He attended North Carolina State University in Raleigh from 1965 to 1969 and received a B. S. degree in chemistry with a minor in mathematics. In June 1969, he began graduate studies at the Georgia Institute of Technology in Atlanta, Georgia under Dr. E. C. Ashby in the area of organometallic chemistry.

In June 1970, he married the former Reenie E. May of Louisburg, N. C. who holds B. S. degrees in chemistry (1969) and science education (1970) from N. C. State University.

In September 1970, he was inducted into the United States Army and served as an enlisted man in the airborne field artillery with Battery B, First Battalion (Abn) 319th FA, 82nd Division stationed at Fort Bragg, N. C.

In June of 1972, he resumed his graduate studies with Dr. Ashby at Georgia Tech.

In November 1973, he coached his wife, Reenie, during the birth of their first child, Edward Garrett Parris.

After completion of his degree at Georgia Tech, George will begin a National Research Council post-doctoral appointment at the National Bureau of Standards at Gaithersburg, Maryland.

George's chief leisure activities are running; which he began in public school, continued by receiving athletic letters with the

N. C. State University cross country team (1966, 1967); and spelunking which he began in 1969 with the Dogwood City Grotto of the National Speleological Society and with which he has visited such caves as Fern Cave in Alabama and Ellison's Cave in Georgia.